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# Peatland-Stream Hydrological and Biogeochemical Connectivity in the James Bay Lowland, Ontario

Meghan Kline
*The University of Western Ontario*

Supervisor
Dr. Brian Branfireun
*The University of Western Ontario*

Graduate Program in Geology
A thesis submitted in partial fulfillment of the requirements for the degree in Master of Science

PEATLAND-STREAM HYDROLOGICAL AND BIOGEOCHEMICAL CONNECTIVITY IN THE JAMES BAY LOWLAND, ONTARIO

(Thesis format: Integrated Article)

by

Meghan Kline

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The School of Graduate and Postdoctoral Studies
The University of Western Ontario
London, Ontario, Canada

Abstract

The Hudson-James Bay Lowlands are the second largest peatland dominated area on the planet, and are expected to be particularly vulnerable to future climate change. Changes in climate will affect peatland hydrology and biogeochemistry, impacting the aquatic ecosystems this region supports, however there is limited information about the hydrology and biogeochemistry of this landscape under current conditions. This thesis focuses on assessing the nature of hydrological and biogeochemical connectivity between a fen and $2^{nd}$ order channel in the Central James Bay Lowland, Ontario. Specifically the study focuses on the role of preferential hydrological flowpaths in the riparian area, such as soil pipes and rivulets. We used water table-discharge relationships to examine the nature of hydrological connectivity between the fen and riparian area and identified thresholds of hydrological connectivity using these relationships. Once the storage thresholds in the near stream depression and fen have been met, peak flow can be generated in the soil pipes and rivulets, this occurs under wet antecedent conditions late in the fall. The study also identified that the riparian area is a likely dominant source of DOC and MeHg despite the extensive peatlands that dominate the upslope region, and that this area has a unique chemical signature from the fen. Furthermore late fall storm events with wet antecedent conditions were found to play an important role in solute transport from the soil pipes, with as much as >60% of the total solute load for one soil pipe occurring during a storm event which had a duration of only 17% of the monitoring period.

# Keywords

Peatlands, James Bay Lowland, Mercury, Methyl Mercury, Carbon, Soil Pipes, Riparian Zones, Hydrological Connectivity.

# Co-Authorship Statement

I hereby declare that I am the sole author of this thesis, except as noted below. I understand that my thesis may be made electronically available to the public.

**Exceptions to sole authorship:**

For all chapters, Dr. Brian Branfireun acted as an advisor, editor, and offered suggestions on scientific content, and the treatment and presentation of data in this thesis. He will be listed as a co-author on any subsequent publication stemming from this work.


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# Table of Contents

# List of Tables

# List of Figures

# 1 Introduction and Literature Review

## 1.1 Climate Change and Northern Catchments

Hydrological changes as a result of climate change have already been observed in northern regions, with potential implications for water quality and quantity (Rouse *et al.,* 1997; Peterson *et al.,* 2002; McClelland *et al.*, 2004; Dery *et al*., 2005; Tetzlaff *et al*., 2013). Changing precipitation patterns, increasing evapotranspiration, and degrading permafrost will continue to alter the nature of hydrological connectivity in northern regions, impacting not only the timing and magnitude of runoff, but also the flowpaths and the proportions of water from different sources (McClelland *et al.*, 2004; Frey and McClelland, 2009; Tetzlaff *et al*., 2013). In Eurasia, discharge from rivers into the Arctic Ocean has increased by ~7% between 1936 and 1999 (Peterson *et al.,* 2002). Increased precipitation and permafrost degradation are both proposed as potential mechanisms to explain this increase in flow (McClelland *et al.,* 2004). In contrast, discharge trends in North America are less consistent; with increased mean annual flows in some northern catchments, but with little change or decreases of flow exhibited by others (Dery *et al*., 2005). This highlights the complexity of the hydrological responses of northern catchments to climate change, and the uncertainty associated with predictions of those responses.

These hydrological changes will in turn influence water chemistry. Many permafrost catchments presently have large contributions from snowmelt and rainfall to streamflow, typically resulting in dilute water chemistry (Carey *et al*., 2013). This dilute chemistry may be altered by future climate change if water tables decline, and degradation of permafrost allows greater interaction between surface and deep mineral groundwater sources potentially resulting in greater concentrations of major ions in stream water (Frey and McClelland, 2009). Dramatic increases in dissolved organ carbon (DOC) fluxes have also been predicted in response to the expected melting of organic matter presently frozen in northern permafrost peatlands if the areas of the north exposed to mean annual air temperatures greater than -2◦C expand (Frey and Smith, 2005). Therefore there is the potential that climate change will have significant implications on both the biogeochemistry of sensitive northern aquatic habitats as well as carbon cycling in these systems. However, there remains some uncertainty about the implications of these changes for stream water chemistry because of the potential for higher discharge to have a diluting effect on the water chemistry of streams, potentially mitigating some of the effects (Frey and McClelland, 2009).

## 1.2 Runoff Generation Processes in Northern Catchments

### 1.2.1 Storage Thresholds in Runoff Generation

Antecedent moisture conditions and bedrock microtopography have been shown to influence runoff timing and magnitude as well as solute transport in catchments in the Precambrian Shield region of northern Canada (Allan *et al*., 1994; Allan and Roulet, 1994). Furthermore, extensive research in this region suggests that storage thresholds play an important role in runoff generation for many northern catchments (e.g. Frisbee *et al*., 2007; Spence *et al*, 2007; Woo and Mielko, 2007; Spence *et al*., 2010, Oswald *et al*., 2011; Phillips *et al*., 2011). Those elements of the landscape that have the lowest thresholds relative to the quantity of water input are the first to contribute to runoff (Spence and Woo, 2006). The areas closest to the channel are therefore not necessarily the first part of the catchment to contribute, and the runoff generated may not necessarily reach the channel if there are storage deficits to be satisfied downslope (Frisbee *et al*. 2007). Storage is often difficult to quantify (see Spence, 2007) and has been measured in a variety of different ways, making comparisons between studies potentially difficult (McNamara *et al*., 2011). The difficulty arises partially because storage can be estimated either indirectly using water balances (e.g. Sayama *et al.,* 2011), or directly by quantifying groundwater, soil moisture, and lake volumes hydrometrically (e.g. Spence *et al*., 2009).

Catchments where storage thresholds are a dominant control for runoff generation can be less resilient to climate change because small changes in temperature or precipitation may dramatically influence the quantities of runoff produced (Carey *et al.,* 2010). At the catchment scale, storage thresholds depend on soil depth and type, bedrock topography, slope, presence of ground frost, and other physical characteristics that control the volume of water that can be stored. (Spence, 2010; Spence and Woo, 2003). Sayama *et al.* (2011) found that median slope angle was the strongest watershed variable that related to the amount of water that a watershed could store, with steeper watersheds being able to store larger volumes of water. Storage torage limits tend to be more distinct in catchments with gentler topography and lower quantities of precipitation, while discharge and precipitation may be more closely coupled in steeper, wetter catchments (Carey *et al*., 2010). This suggests the particular importance of storage in lowland environments. Spence (2010) described the growing recognition that storage thresholds play an important role in runoff generation for many northern catchments. It has been demonstrated that the extent of the contributing area does not expand and contract continuously, as was previously thought, but consists of the discrete parts of the catchment that have met their individual storage capacities, and the extent of the contributing area can therefore behave very dynamically (*Ibid*).

Antecedent water levels, storage availability, and the quantity of rainfall all influence how much of the catchment is contributing during a given storm event, making runoff generation highly dynamic and potentially localized. The availability of storage in depressions and micro-basins can decrease the contributing area of a catchment under dry conditions when these depressions capture and store water, thereby preventing upslope areas from contributing to runoff. For example in the Precambrian Shield, Frisbee *et al.* (2007) observed that storage deficits in a micro-basin resulted in the reduction of the contributing area by 30% when water levels were below a threshold level.

Furthermore, runoff generation can be dominated by a disproportionately small portion of the catchment. For example, Oswald *et al.* (2011) found that although bedrock depressions comprised only 22% of the catchment they contributed approximately 71% of discharge. Small inputs of water in parts of the catchment that are close to meeting storage thresholds can generate disproportionate quantities of runoff. Antecedent storage capacity in individual parts of the catchment is therefore more important than the absolute volume of water input at the event scale (Zehe *et al.*, 2005).

The influence of individual elements of storage such as depressions, micro-basins, and lakes on runoff generation depend on their position within the catchment because downstream features can attenuate runoff from those upstream, especially when these downstream features have greater available storage (Frisbee *et al*., 2007; Woo and Mielko, 2007; Phillips *et al*., 2011). These features can moderate how much of the contributing area is able to provide runoff to the channel (Spence *et al*., 2009). For example, for chains of small lakes in the semi-arid subarctic, full hydrological connection along the channel can only occur when the water levels of all the lakes are above their outflows (Woo and Mielko, 2007). Individual lakes reach the level of their outflow at different times and therefore also start to contribute at different times; when larger lakes are located downstream they can effectively attenuate flow along the channel, because they will take longer to reach their storage thresholds (*Ibid*). This effect is not limited to small headwater catchments since lake storage deficits have also been shown to be a major control on runoff response for higher order northern rivers such as the Yellowknife River (Spence *et al*., 2007).

### 1.2.2 Preferential Flow in Soil Pipes and Macropores

Storage thresholds also influence the magnitude and timing of runoff contributed by specific runoff generating mechanisms such as macropores and soil pipes. Soil pipes have been demonstrated to be important for runoff generation on subarctic permafrost slopes (Carey and Woo, 2000), subarctic wetlands (Woo and Dicenzo, 1987), and more temperate blanket peatlands (Holden and Burt, 2003). Macropore flow is often a threshold-mediated runoff generation process, with soil pipes only flowing once the water table has risen above the level of the soil pipe (Spence, 2010), however pipe networks can be complicated, extensive, and occur across different elevations (Holden, 2004). Therefore these threshold levels for flow initiation are not always obvious, and perennial soil pipes can continue to flow even under relatively dry conditions (Holden and Burt, 2002). During snowmelt, the presence of the frost table prevents drainage and can make it easier to meet the thresholds for flow, resulting in the importance of soil pipes in northern catchments under these conditions (Carey and Woo, 2000).

In addition to facilitating preferential flow of water, soil pipes have been found to transport significant amounts of solutes, sediment, and energy (Jones, 1994; Carey and Woo, 2002; Holden, 2006; Holden *et al*., 2012). Soil pipes can therefore influence stream water chemistry, contributing to acidification, or transport of nutrients, metals, and carbon depending on the nature of the catchment (Jones, 1994, Holden, 2006; Hill, 2012, Holden *et al*., 2012). Soil pipes are dynamic features that can play an important role in geomorphological evolution (Jones, 1994) and northern catchments with soil piping can have complex and dynamic interactions between surface water, rills, soil pipes, and runoff (Carey and Woo, 2000). In permafrost catchments the ability of preferential flowpaths to enhance the advection of heat, as well as sediment, means they can encourage the thaw of the active layer, and also lead to subsidence; thereby playing an active role in the geomorphological development of permafrost landscapes (Andersland and Ladanyi, 1994). In cold environments, macropores may form by soil contraction and as a result of drying and cracking promoted by upward vapor fluxes driven by large temperature gradients between the soil and the air during winter (Lachenbruch, 1963; Santeford, 1979; Smith and Burn, 1987).Typically soil pipes form where there is a layer with high lateral permeability just above an interface with a sharp reduction in vertical permeability (Jones, 1994). Many permafrost catchments have frozen mineral soils overlain by more permeable organic layers, providing ideal circumstances for pipe formation (Carey and Woo, 2002).

The contributions from soil pipes to streamflow have been estimated to be as much as 30% depending on antecedent conditions (Holden, 2004). Their importance can vary seasonally, with soil pipes contributing different proportions of streamflow at different times of the year. In blanket peat catchments they have been found to be particularly important under low flow conditions (Holden and Burt, 2002), whereas in permafrost environments soil pipes are mostly ephemeral and only flow during snowmelt and very large summer storms (Carey and Woo, 2000). On these permafrost slopes, soil pipes may contribute 20% of flow during snowmelt, whereas summer runoff is dominated by slower flow through the soil matrix (Carey and Woo, 2000). These changes in the relative importance of different runoff generating processes can in turn influence how hydrologically connected and efficient a catchment becomes at that time.

### 1.2.3 Catchment Hydrologic Efficiency and Connectivity

Catchment hydrologic efficiency, or the ability to turn precipitation or snowmelt into runoff, can be defined as the ratio between discharge and storage (Spence *et al*., 2010). Spence *et al*. (2010) distinguished between topographic basin storage, which only related poorly to streamflow, and hydrologically connected storage, which had a strong hysteretic relationship with streamflow. They suggested that these storage-discharge curves can be used to determine whether the functional state of the catchment is storing or contributing (*Ibid*). Catchment efficiency is relevant to understanding how northern catchments will be impacted by future climate change because catchments that efficiently translate precipitation or snowmelt into runoff are less resistant to changes in quantity or phase of precipitation, compared to catchments that store water over longer periods of time and release it gradually (Carey *et al*., 2010).

Bracken and Croke (2007) defined connectivity as the ability to transfer water between landscape elements. They described this capacity as a dependent variable controlled by both static and dynamic factors. Static factors reflect spatial variability in the physical characteristics of the catchment, such as topography or soil properties, that influence runoff. Dynamic factors include both short-term changes, such as variations in rainfall inputs and antecedent moisture conditions, and long-term changes, such as those resulting from land use change (*Ibid*). The importance of connectivity as the threshold mediated coupling of landscape elements to generate runoff and facilitate solute transport is being increasingly recognized in diverse environments (e.g. McDonnell, 2003; Quinton *et al.*, 2003; Ambroise, 2004; Bracken and Croke, 2007; Spence, 2010). Hydrological connectivity plays a pivotal role in defining hydrological, biogeochemical, and ecological dynamics between terrestrial and aquatic ecosystems (e.g. Pringle, 2003; Stieglitz *et al.*, 2003; Burt and Pinay, 2005; Bracken and Croke, 2007). Hydrologic simulations have suggested that for much of the year water draining through a catchment may be spatially isolated, and upland and lowland areas only rarely become hydrologically connected, such as during storm events when antecedent moisture conditions are high (Stieglitz *et al.*, 2003). As the degree of connectivity changes with season, the part of the landscape exporting solutes changes as well; for example nutrient export may be limited to the near-stream area during the low-connectivity growing season (*Ibid*). Gatekeeper elements such as intervening lakes or riparian wetlands can maintain or disrupt the connectivity of upstream elements (Phillips *et al.*, 2011). Processes that increase or decrease hydrological connectivity can impact the ecological integrity of the landscape (Pringle, 2003).

## 1.3 Role of Riparian Zones in Mediating Hydrological Connectivity

Riparian areas are the interface between terrestrial and aquatic ecosystems, typically possessing steep gradients for plant communities, soils, and hydrology (Gregory *et al.*, 1991). Riparian zones are frequently zones of mixing as a result of convergent hydrological flowpaths near the channel that bring together water from different sources, and potentially complementary reactants. In addition, biogeochemical processes within the near stream zone may result from the steep gradients in local characteristics of the near stream area such as soil type or the degree of saturation (McClain *et al.*, 2003; Vidon *et al.*, 2010; Burt and Pinay, 2005). Streams may strongly reflect the riparian zone chemistry as there is a potential for water chemistry to be "reset" in the near stream area (Robson *et al.,* 1992; Cirmo and McDonnell, 1997; Burt and Pinay, 2005). For example, in their mixing analysis Burns *et al.* (2001) found that water from upslope was mixing in the riparian aquifer, which was the dominant contribution to streamflow. In some cases the mixing may be conservative and the chemistry can still reflect upslope areas (Burns *et al.*, 2001). However, when riparian aquifers provide storage, thereby lengthening the residence time, the near stream area can be a site of biogeochemical reaction between storm events; resulting in a unique riparian chemical signature (Hooper *et al.*, 1998). By contrast, under peak flow conditions the contribution of water and solutes from the hillslope may overwhelm or bypass the riparian area altogether (McGlynn and McDonnell, 2003; Inamdar, 2006). Mixing processes in riparian areas can be complex and isotope and tracer studies report that full mixing cannot be assumed; instead the degree and spatial extent of mixing depend on catchment properties and vary over time, presenting challenges for accurately modelling the influence of riparian zones on stream water quality (Inamdar, 2006).

Since the hillslope is considered the basic landscape element in many environments, much of the hydrologic literature has focused on the coupling between the hillslope and the channel, and the potential for the floodplain or riparian zone to facilitate or impede this coupling (Burt and Pinay, 2005; Bracken and Croke, 2007). Hydrologic coupling between hillslope and riparian areas must occur in order to deliver solutes from the upland to the channel (Hooper *et al*., 1998; Burt and Pinay, 2005; McDonnell and McGuire, 2010; McGlynn and McDonnell, 2003) However, as a result of threshold behaviour, in some cases the hillslope may only be rarely coupled with the channel (Tromp-van Meerveld and McDonnell, 2006). Upslope-riparian interactions such as continuity of connection with the upland, magnitude of water table fluctuations, and the potential for flow reversals, which in turn influence biogeochemistry, are determined by local characteristics such as slope and surficial geology (Vidon and Hill, 2004). Cirmo and McDonnell (1997) note the dramatic change in hydrological conditions because of the transition between the steep hillslope and the gently sloping near stream area. However, riparian zones have been found to play similarly important roles in catchments lacking these dramatic changes in topographic relief (Burt and Pinay, 2005). In these catchments with less topographic relief the riparian influence on water chemistry is dominated by biological rather than geochemical processes (*Ibid*).

Much of the interest in the biogeochemical processes of riparian areas has been motivated by recognition of the ability of riparian forests to attenuate contaminants such as $NO_3^-$ from agricultural runoff (Lowrance *et al.,* 1997). Studies have found that nitrate concentrations can decrease by more than 90% as they flow through riparian areas (Hill, 1996; Dosskey, 2001). This has led to riparian zones being described as buffers and as sinks for certain contaminants due to the presence of zones of elevated rates of biogeochemical reaction within them (McClain *et al*., 2003). Although much of the research has focused on the capacity of riparian areas to buffer certain contaminants, for other contaminants, such as methyl mercury (MeHg), they can actually contribute more of the contaminant than upland areas do (Bishop *et al.,* 1995; McClain *et al.,* 2003; Vidon *et al*., 2010). Biogeochemical activity may be promoted by the steep ecological gradients inherent in the intermediate position of riparian areas between terrestrial and aquatic environments (Vidon *et al.,* 2010). Many riparian environments are classified as wetlands such as riparian bogs, fens and swamps (NWWG, 1997), due to higher water tables in the near stream area that result in development of hydric soils and the growth of hydrophilic plants (Cowardin et al., 1979).

## 1.4 Northern Wetlands

Wetlands are particularly common between the latitudes 50-70 degrees north, and play an important role in the hydrology of many northern catchments (Aselmann and Crutzen 1989). Wetlands have been defined as land that is saturated for long enough to promote development of hydric soils and support biota that are specifically adapted to wet conditions (NWWG, 1997). Peatlands are a type of wetland with a layer of organic matter at least 40 cm thick (NWWG, 1997). Peatlands develop well in areas of low topography and poorly drained soils or permafrost where the climate allows plant growth and precipitation outweighs evapotranspiration (Bleuten *et al*., 2006). Organic matter accumulates in peatlands as a result of biogeochemical conditions, such as low redox potential, that impede the decomposition of plant material (Clymo, 2008). Peatlands are partially self-regulating environments where water table levels and peatland aggradation are functions of a complex interplay between ecological and hydrological processes (*Ibid*.).

Bogs and fens are the two dominant types of peatlands in Canada (NWWG, 1997). They are distinct in terms of both hydrology and vegetation. Bogs are peat-accumulating wetlands that receive water and solutes from atmospheric sources, resulting in dilute water chemistry. They are typically dominated by black spruce, Sphagnum mosses and ericaceous shrubs (*Ibid*). By contrast fens may receive water and solutes from both atmospheric sources and groundwater sources that supply higher concentrations of dissolved minerals and have higher pH in pore waters than bogs (Bleuten *et al*., 2006). Fens support vegetation that requires greater nutrient supplies such as tamarack, graminoids and brown mosses (NWWG, 1997). Fens are also generally wetter than bogs, with greater fluctuations in water table elevation, in nutrients, and in peat composition, resulting in a greater variability in the species that they can support (Riley, 2011).

### 1.4.1 Peatland Hydrology

Peatlands have conventionally been hydrologically conceptualized in terms of two layers; the upper layer or *acrotelm*, and the lower layer or *catotelm*, with the base of the *acrotelm* defined by the lowest level the water table reaches under dry conditions (~10-50cm below ground surface) (Clymo, 1984). Decomposition rates tend to be faster in the aerobic *acrotelm*, compared to the deeper anaerobic *catotelm* where the influx of oxygen is slower than its consumption by microorganisms. The boundary between them may reflect the collapse of plant structure at that depth, and the resultant increase of bulk density and decrease of porosity (Clymo, 2008). The *acrotelm* therefore has dramatically higher hydraulic conductivity and porosity than the *catotelm,* and dominates rapid flow, while the *catotelm* supplies slow groundwater flow (Chason and Siegel, 1986).

Despite the widespread use of these terms since they were originally coined in Russian by Ivanov (1953), their ability to adequately describe peatland ecohydrological processes has recently been called into question (Morris *et al*., 2011). This is in part because although depth does exert a powerful control on peatland ecohydrological variables such as saturation and redox potential, the use of a simple one-dimensional diplotelmic model is inadequate to describe the significant influence of horizontal heterogeneity on water, solute, and energy transport in peatlands (*Ibid*.). As an alternative, Morris *et al*., 2011 propose that more descriptive language could be used in describing boundaries and layers in peatlands, such as oxic/anoxic, and that peatlands may more constructively be conceptualized according to the framework of biogeochemical and hydrological hot and cold spots. Biogeochemical hot spots have been defined by McClain *et al.* (2003) as patches with disproportionately high reaction rates compared to their surroundings, and are recognized as being especially important at the interface between terrestrial and aquatic environments, and cold spots would imply the inverse. Conceptualizing peatlands this way would allow for more flexibility in describing horizontal changes in ecohydrological variables in addition to variation with depth (Morris *et al*., 2011).

In northern peatland complexes, bogs and fens serve in distinct hydrological roles, with fens serving primarily to transmit water through the landscape while bogs generally act to store water, except under very wet conditions (Quinton *et al.,* 2003). Partly as a result of the domed shape of bogs, the direction of flow is typically from bogs to fens, with flow from bogs concentrated along fen water tracks (Glaser *et al*., 1990; Glaser, 1992; Price and Maloney, 1994). Compared to bogs, fens are more integrated into the overall drainage system because they are more sensitive to the extent of upland contributions and are responsive to upland hydrology, and in turn, fens influence basin runoff more (Carter, 1986; Price and Fitzgibbon, 1987; Price and Maloney, 1994)

Peatlands have the ability to minimize high flows and to delay hydrologic response by providing depression and detention storage in a low gradient environment (e.g. Price and Maloney, 1994). Storage availability in peatlands is thought to influence the timing and magnitude of runoff in lowland northern landscapes (Pietroniro *et al.,* 1996). However, this primarily occurs under drier conditions when wetland storage capacities have not been met, since once storage is satisfied wetlands no longer attenuate flow to the same degree (Price and Maloney, 1994; Quinton and Roulet, 1998; Hayashi, 2004). Therefore, distinct connected and disconnected hydrological phases have been identified under wet and dry conditions in northern wetland systems (Quinton and Roulet, 1998; Branfireun and Roulet, 1998)

In patterned wetlands, Quinton and Roulet (1998) found that the availability of storage in pools and depressions controls the degree of connectivity in the wetland, and therefore its capacity to generate runoff. Under dry conditions water would go to satisfy depression storage, whereas during wet conditions water inputs would contribute to runoff generation. This led to the identification of two distinct phases of wetland hydrology: connected (under wet conditions) and disconnected (under dry conditions) (*Ibid*). When peatland pools are disconnected, they may contribute little to runoff, and primarily contribute to evaporation (Price and Maloney, 1994). Typically, northern peatland complexes are most connected during the spring because of limited storage due to frozen ground and abundant water inputs from the melting snow (Bowling *et al*., 2003). At the start of snowmelt a storage deficit may exist from the previous year that must be satisfied before connectivity increases and runoff is generated. The size of this deficit reflects how wet conditions were at the start of the winter, as well as the size of the winter snowpack (*Ibid*). As conditions become drier during the summer, individual peatlands can become isolated from the basin's drainage system, as reflected by shifts in chemistry (Hayashi *et al.*, 2004). As a result, during the summer, peatland-draining streams may show minimal response to precipitation events (Bowling *et al.*, 2003).

Branfireun and Roulet (1998) also identified two hydrologic regimes that describe connectivity in an upland-peatland system. In their study the upland became decoupled from the peatland under dry conditions, such that only baseflow was contributed from the upland area. Under wetter conditions more direct coupling was facilitated by the development of a zone of saturation above the upland-peatland interface. Under dry conditions smaller quantities of runoff was generated quickly in the peatland, while wet conditions produced a higher magnitude and sustained response with contributions from both the peatland and upland areas. Devito *et al*. (1996) found that geology was an important control on upland-wetland connectivity in valley-bottom conifer swamps in the Canadian Shield. Surficial geology strongly influenced the temporal dynamics of upland-wetland connectivity. In the catchment with thick till the connection between the upland and the swamp was continuous, facilitating baseflow contributions during the dry season. By contrast, where the till was thinner, the connection was ephemeral and baseflow ceased under dry conditions.

### 1.4.2 Peatland Biogeochemistry

#### 1.4.2.1 Carbon

While peatlands make up only 3% of the Earth's land surface, they store 15-30% of the world's soil carbon (Limpens *et al*., 2008). The layer of organic matter in peatlands grows as long as the rate of accumulation outpaces the rate of decomposition (Clymo, 1984). Water saturated conditions with low redox potential facilitate the slow rates of decay of plant litter that results in peat formation (Bleuten *et al.,* 2006). It is estimated that boreal peatlands store between 270 and 370 Tg C (Turunen *et al.,* 2002). Although undisturbed peatlands act as sinks for carbon dioxide, they are sources of DOC and methane (Blodau, 2002).

The balance between sequestration and emission of carbon can shift depending on climate conditions (Moore *et al*., 1998; Belyea and Malmer, 2004). Decomposition of organic matter into end products such as carbon dioxide, methane, and DOC results from the interaction between microbial activity and the availability of electron acceptors and nutrients (Limpens *et al*., 2008). Decomposition rates are sensitive to redox conditions, which can in turn be influenced by fluctuations in the water table. The thickness of the acrotelm is an important determinant of the rate of organic matter decay, because it controls the residence time of the plant material under aerobic conditions (Belyea and Malmer, 2004). Episodes of rapid warming and drying due to climate change are generally expected to increase carbon exports from peatlands (Oechel *et al.,* 2000). Since anaerobic decomposition produces methane while aerobic decomposition yields carbon dioxide, changes to water table can also shift the balance between methane and carbon dioxide production and fixation (Dise, 2009). Since the balance between carbon oxidation and methanogenesis depends on complex relationships between vegetation type, hydrology, climate, depth, and microbial activity, it is difficult to make general predictions of how peatland carbon cycles might respond to climate change (Limpens *et al*., 2008; Moore *et al*., 1998). Furthermore, peatlands are partially self-regulating systems, and therefore have some resilience to environmental change by adjusting over time in response to climate-driven changes. This makes long-term observations particularly important (Dise, 2009).

Dissolved organic carbon influences acid-base chemistry, metal complexation, water colour, biogeochemical cycles, and productivity of downstream aquatic ecosystems (Pastor *et al*., 2003; Limpens *et al*., 2008). Aquatic fluxes of DOC from boreal and temperate peatlands typically range between 1-50 g DOC $m^2$/yr (Dillon and Molot, 1997). Because much of the solute transport in peatlands occurs through hydrologically responsive shallow flow pathways, overland flow, or soil pipes, the export of DOC from peatlands can be elevated during storm events (Carey and Woo, 2000; Holden and Burt, 2003; Holden *et al*., 2012). Hydrology also controls reaction rates, for example rapid lowering of water tables can result in elevated DOC production and concentrations at depth, because when the water table is not at the peat surface there may be less inhibition by the accumulation of $CO_2$ and $CH_4$ (Blodau and Moore, 2003; Blodau *et al*., 2004). Sustained droughts that persist for at least 3-5 years can influence pore water chemistry in peatlands, potentially resulting in increased DOC export if subsequent flushing occurs (Siegel *et al.,* 1995).

#### 1.4.2.2 Mercury

Numerous studies have cited the importance of wetlands in the global mercury (Hg) cycle (e.g. St Louis *et al.,* 1994; Branfireun *et al.,* 1996; Driscoll *et al*., 1998; Selvendiran *et al*., 2008). Wetlands have been identified as sinks for total Hg but sources for MeHg to downstream environments (e.g. St Louis *et al*., 1994; Branfireun *et al*., 1996; Allan and Heyes, 1998; Driscoll *et al.,* 1998,). Since Hg binds to sulfur-groups in dissolved organic matter, carbon and Hg accumulation and transport are closely linked (Skyllberg *et al*., 2000; Grigal, 2003). Up to 66% of total Hg can be immobilized by binding with humic acids in peat (Zaccone *et al*., 2009). In the absence of local point sources, the majority of Hg that is found in remote northern wetlands has been transported from distant sources and deposited from the atmosphere (Fitzgerald, 1998). The Hg bound in peatlands, specifically ombrotrophic bogs, can act as archives of past atmospheric Hg deposition rates (Bindler, 2003; Zaccone *et al*., 2009).

Methyl Hg is a potent neurotoxin and more ecologically harmful species of Hg, that biomagnifies more readily than inorganic Hg (Ullrich *et al.,* 2001). Inorganic Hg is typically converted to MeHg by microbially mediated methylation, commonly by sulphate reducing bacteria (*Ibid.*). In peatlands, the highest concentrations of MeHg are typically found at the boundary between aerobic and anaerobic conditions in the peat pore water (Heyes *et al*., 2000). Dynamic water tables that result in fluctuations between anaerobic and aerobic conditions have been proposed as a primary control on methylation timing, magnitude, and location (Heyes *et al*., 2000; Branfireun and Roulet, 2002; Branfireun, 2004; Vidon *et al*., 2010). Additions of sulphate have been found to stimulate Hg methylation in peatlands, which are typically sulphate-limited (Branfireun *et al.,* 1999). Furthermore, mesocosm scale experiments led to the determination that combined additions of sulphate and labile carbon stimulated methylation more than additions of sulphate alone (Mitchell *et al*., 2008).

Mercury methylation does not seem to occur uniformly within peatlands, but instead appears to be concentrated in distinct zones that are located either at sites of groundwater upwelling (Branfireun and Roulet, 2002) or at the interface between peatland and upland areas (Mitchell *et al*., 2008). In both of these examples, convergent flowpaths result in the delivery of reactants (labile carbon, sulphate, nutrients) to conditions conducive to methylation (anaerobic). Mercury methylation in peatlands has been demonstrated to be sensitive to microtopography as well, with shallow hollows having higher MeHg concentrations than hummocks and deep hollows (Branfireun, 2004). This may reflect the impact of important differences in temperature, hydrology, and biogeochemistry on microbial activity even at this very small scale, and suggests a high level of heterogeneity in the Hg methylation process in peatlands (*Ibid*.).

In order for zones of elevated Hg methylation to impact downstream ecosystems they must be coincident with transport mechanisms that can deliver solutes from the terrestrial to the aquatic ecosystem (Vidon *et al*., 2010). Therefore it is the hydrological connectivity between the methylating parts of the wetlands and the stream that determines the stream load of MeHg (Bishop *et al*., 1995; Shanley *et al*., 2008; Vidon *et al*., 2010). This hydrological connectivity changes seasonally and depending on storm events. For MeHg the loading in the stream depends on the interaction of flow dynamics with the timing of the biologically mediated methylation process and for this reason methyl and total Hg concentrations in streams have been found to peak at different times of year. Peak MeHg export can occur in summer storms and the autumn as a result of mobilization of elevated MeHg that accumulated over the growing season by episodes of higher flows (e.g. Babiarz, 1998; Selverindan *et al.*, 2008). By contrast, export of total Hg is often dominated by spring snowmelt, when the greatest flows are usually experienced (e.g. Mitchell *et al*., 2008; Babiarz, 1998; Scherbatskoy *et al*., 1998).

## 1.5 Vulnerability of the Hudson Bay Lowlands to Climate Change

The Hudson Bay Lowlands, which includes the James Bay Lowland, (HJBL) are the third largest expanse of wetland in the world, the second largest peatland area, and are located within the world's largest intact boreal landscape (Riley, 2011). This region of Canada's North is particularly vulnerable to climate warming because of the key role that sea ice plays in cooling the local climate (Gough and Wolfe, 2001). Predictions for the Hudson Bay region's climate include longer, warmer summers, and shorter, warmer winters. If warming temperatures reduce the seasonal sea ice coverage of the Hudson Bay, the open water could play a moderating role resulting in still warmer winters (*Ibid*). Overall, precipitation is expected to increase, especially in the winter, or stay constant (IPCC, 2007). However, Rouse *et al.* (1991) predict that the combination of warming climate and the feedback effect of diminished sea ice will result in a 5% increase in evapotranspiration. Discharge from some of the rivers draining into the Hudson Bay has already declined by ~10% between 1964 and 2000 (Dery *et al.,* 2005). Declining flow and earlier snowmelt have been also observed in the Churchill-Nelson rivers (Westmacourt and Burns, 1997). Declining flow in these rivers suggests that the increased evapotranspiration counteracts the increased precipitation and overall the region may be becoming drier.

## 1.6 Rationale, Aims and Objectives

Concerns about the implications of land use and climate changes on hydrology and biogeochemistry in the HJBL have motivated recent research efforts in this area. Residents of communities near the James Bay coast may be exposed to elevated concentrations of MeHg in fish from this region, despite a lack of local point source of Hg (Girard and Dumont, 1995). Furthermore, carbon and Hg dynamics within this landscape are believed to be sensitive to predicted climate changes, but there is limited baseline information available.

The peatland and river systems have been described as two discrete and largely isolated flow systems, with limited interaction (Riley, 2011). Richardson *et al*. (2012) drew attention to the role near stream fens play in defining catchment efficiency, but there is poor understanding of how these fens interact with the channel. This is a key step for understanding runoff generation in this landscape, and the loading of DOC and Hg to aquatic ecosystems. Research in diverse environments has highlighted the importance of riparian areas to biogeochemical reactions and transport processes in general (Vidon *et al*., 2010), as well as specifically for loading of MeHg to streams (Bishop *et al*., 1995). However, there is limited information on riparian areas in the extensively peatland-dominated landscape of the HJBL, where the entire 'upland' area consists of wetland complexes, and it is unclear whether the understanding from other landscapes would be transferable to this environment.

Field surveys of a riparian area located near an established research site in a bog to fen transition were performed during the 2011-2012 field seasons. It was observed that the peat thinned considerably within 100m of the channel, and that a complex network of small rivulets, soil pipes, and small depressions with pooled water existed in the transition between the fen and the channel. These observations prompted further investigation into how these features might influence hydrological connectivity and fluxes of carbon and Hg from the fen to the channel. Intensive monitoring was performed during the 2012 fall wet-up period, in order to facilitate the development of a more appropriate conceptual model of fen to stream flow mechanisms and solute transport. The first research chapter of the thesis (Chapter 2) focuses on the hydrological connections in terms of 1) timing and magnitude of runoff response, 2) storage-discharge relationships (using water table as a proxy for storage) between the fen and near stream depression and soil pipes and rivulets, and 3) determining the sources and flowpaths for water being transported through the riparian area by these preferential pathways using natural tracers. The second research chapter of the thesis (Chapter 3) builds on the observations of hydrological connectivity in the riparian area from Chapter 2 by examining the implications for Hg and carbon export to the stream. This chapter 1) compares the concentrations of MeHg, total Hg, and DOC in different compartments along the fen-stream transition, 2) explores storm concentration dynamics for these solutes, 3) and calculates approximate loads and fluxes of carbon and Hg transported by soil pipes and rivulets during the autumn.

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# 2 Peatland-Surface Water Hydrological Connectivity in the Canadian Subarctic – the Critical Role of the Riparian Zone

## 2.1 Introduction

### 2.1.1 Hydrological Connectivity

The nature of hydrological connectivity between terrestrial and aquatic ecosystems governs water flux, hydrological response, and many biogeochemical cycles (Steigletz, 2003). The degree of connectivity between landscape elements (such as hillslopes, riparian areas or bedrock depressions) has been demonstrated to have profound implications for water quantity and quality because connectivity determines how much water is contributed to surface waters by different sources with potentially different chemistries (e.g. Quinton and Roulet,1998; Stieglitz *et al.*, 2003; Ali *et al.*, 2010; Oswald *et al.*, 2011; Phillips *et al.*, 2011).

Since dynamic factors that influence connectivity, such as rainfall, are functions of climate, the interactions between dynamic and static factors of landscapes must be clarified in order to predict the consequences of changes in climate for changes in connectivity and the resulting impact on water quantity and quality. Hydrologic connectivity has been well studied in temperate forested hillslopes. However, in remote northern regions that are particularly vulnerable to climate change, such as the peatlands of the HJBL, there is limited data on the nature of hydrological connectivity. Understanding the mechanisms of connectivity in northern peatlands is important because as much as ~75% of runoff can occur during a connected phase which lasts only~14% of the time (Quinton and Roulet, 1998).

Local-scale studies provide insight into controls on hydrological response, and ensure the correct frameworks and parameterization of both conceptual and numerical models. McDonnell *et al.* (2007) argue that connectivity is an emergent property, reflecting the connection between different landscape elements, and represents a way to account for small-scale heterogeneity in the parameterization of larger scale models. Catchment scale work has taken advantage of the information that storage-discharge relationships provide about connectivity to develop process-based descriptions of catchment behaviour, because this approach is applicable across scales (Spence, 2007; Kirchner, 2009; and Oswald *et al.*, 2011). One way toward parameterization of the heterogeneous behaviour of catchments is to establish the relationship between small-scale heterogeneity and the degree of connectivity (McDonnell *et al.*, 2007). Despite the importance of process-based empirical studies of catchments, such work remains a significant challenge in remote peatland-dominated regions such as the HJBL, where few studies have been done and models from other landscapes may not be applicable.

### 2.1.2 Northern Peatlands and the Hudson Bay Lowlands

The HJBL in central Canada are the third largest expanse of wetland in the world, and are located within the world's largest intact boreal landscape, but very little is known about the hydrology of this landscape despite recognition of the ecological significance of the aquatic habitat that it supports (Riley, 2011). This region is also particularly vulnerable to climate warming, the effect of which is exacerbated by diminishment of the sea-ice that helps to cool the local climate (Gough and Wolfe, 2001). Bogs and fens account for approximately 60% of the land cover of the HJBL, while swamp, woodlands, and forests make up only 15% (Riley, 2011). Fens are concentrated adjacent to some of the river channels in the HJBL (Richardson *et al.*, 2012). Research in northern peatlands has enhanced our understanding of connectivity between bogs, fen water tracks, and within the fens themselves. Quinton and Roulet (1998) described how hydrologic connectivity within patterned fens regulates their ability to transmit or store water. This depends on the availability of storage in pools and depressions. They identified two distinct phases of wetland hydrology: connected (under wet conditions) and disconnected (under dry conditions).

Two distinct hydrologic systems have been described in the HJBL; the surficial peatlands, and the deeply incised river networks thought to be dominated by contributions from bedrock aquifers (Riley, 2011). However, Orlova and Branfireun (2014) have recently demonstrated that the peatlands are a dominant source of water to tributary streams at a range of catchment sizes in the Central James Bay Lowland, consistently contributing 53-67% of streamflow, with groundwater making up 20-40% of flow depending on catchment size and season, while the remainder consisted of snowmelt and rain. Furthermore, near-channel fens play an important role in the hydrologic response of some tributary streams and rivers in the HJBL (Richardson *et al.,* 2012). Unfortunately there is a lack of empirical information about the nature of the connectivity between these fens and the adjacent streams. As discussed above, this knowledge is required to predict the impacts of climate change on the water quality and quantity, and is of particular importance in these northern, peatland-dominated systems that are likely to be subjected to extreme climate change over the next century (Rouse *et al.,* 1997).

### 2.1.3 Hillslope-Riparian-Stream Systems as a Model for Studying Hydrological Connectivity

There are many examples of these kinds of empirical process-based investigations of hillslope-riparian zone-stream hydrological connectivity in the hillslope hydrology literature (e.g. McDonnell *et al*., 1998; Burns et al., 2001; Chanat and Hornberger, 2003; McGlynn and McDonnell, 2003; Jencso *et al.,* 2009). There is great variability in the nature of the response and the dominant processes of runoff generation for different hillslopes (Sivaplan, 2003), however; many studies agree on the importance of the riparian areas in moderating runoff generation and solute transport (eg: Hornberger *et al*., 1994; McDonnell *et al.,* 1998; McGlynn and McDonnell, 2003; Inamdar and Mitchell, 2006). Riparian zones can have a disproportionately large influence on the timing and magnitude of runoff, relative to their size. During smaller storm events they may dominate the entire event response (84-97% of storm runoff) with only a small fraction of runoff coming from the hillslope (McGlynn and McDonnell, 2003). In larger storms, the hillslope makes a larger overall contribution during the falling limb, but the riparian area still dominates the rising limb (McDonnell *et al*., 1998; McGlynn and McDonnell, 2003). Storage can be satisfied more easily in riparian areas and result in the disproportionately large contribution to runoff from riparian areas because riparian areas typically have higher water tables than the hillslopes (McDonnell *et al*., 1998). In mountainous regions, topography influences hillslope to riparian water table connectivity, which determines run-off quantity (Jencso *et al*., 2009). Riparian areas can also have a unique chemical signature, distinct from the hillslope, that is sometimes better represented in the stream chemistry than the signature of hillslope is (Hooper *et al.*, 1998; Burns *et al*., 2001; McGlynn and McDonnell, 2003), indicating that they can regulate not only the quantity but the quality of runoff.

### 2.1.4 Objectives

As important transmitters of water, fen peatlands in northern ecosystems are expected to regulate water quantity and quality in surface streams and rivers. Understanding the nature of the hydrological connection between fens and adjacent streams is critical if we are to be able to model and predict the effects of climate or land use change in the north. Therefore, the objective of this study was to build on the findings of other studies of northern fen peatland hydrology and apply the conceptual framework of the hillslope-riparian zone-stream literature to describe the hydrological connectivity of a northern fen peatland-stream system. A simple assumption would be that the flow of water to the stream is dominated by seepage through the riparian area from the fen driven primarily by changes of water table elevation in the fen. Our work helps to evaluate the appropriateness of this assumption. Specifically, our objectives were to:

1) quantify the timing and magnitude of event runoff contributions from a patterned fen to an adjacent stream via surface and near-surface pathways under a range of antecedent water table positions,
2) explain these dynamics in terms of storage-runoff relationships among contributing sub-watershed compartments (fen, riparian zone) using water table as a proxy for storage,
3) use isotopic and geochemical tracers and a mixing model approach to quantify the runoff contributions from hypothesized end-members (fen, riparian surface soils, shallow groundwater, precipitation) and characterize the hydrochemistry of the riparian area.

## 2.2 Site Description

The research site is located at (52.83˚ N, 83.93˚ W) in the Central James Bay Lowland of Northern Ontario, Canada, along a stretch of Tributary 5, a 2$^{nd}$ order tributary of the

Nayshkootayaow River, which is itself a tributary of the Attawapiskat River (Figure 2-1). This site lies within the HJBL; the second largest peatland dominated area in the world, covering approximately 250,000 $km^2$ (Riley, 2011). The study site is categorized as humid high boreal with mean daily maximum temperatures in July between 20-21$^{\circ}$ and an annual precipitation of 610–660 mm, and is within the zone of discontinuous permafrost (Riley, 2011).

In this area, the Precambrian Canadian Shield is overlain by thick Paleozoic carbonate deposits, which have evolved karstic features in some areas (Cowell, 1983). The Wisconsinan and earlier glaciations deposited isolated glaciofluvial sediments and multiple units of carbonate rich tills (Dredge and Cowan, 1989). Isostatic depression of the Hudson Bay area by the Laurentide Ice Sheet facilitated a late-glacial marine transgression known as the Tyrell Sea (Lee, 1960). The Tyrell Sea blanketed the till with thick, low permeability marine sediments, resulting in a landscape with an extremely low topographic gradient of 0.57 m/km and poor drainage (Riley, 2011). These characteristics help maintain high water tables and this facilitated the development of the extensive peatland deposits that cover the surface of the HJBL. Peat accumulated to a thickness of ~ 1.8 to > 2.2 m over much of the interior (Riley, 2011).

The study site is located between a ~ 6 km long patterned fen and the stream. The average topographic gradient along the fen is ~ 0.0013 while the slope of the riparian area from fen to channel is ~ 0.01. The topographic gradient becomes steeper approximately 400 m from the channel, beyond this break in slope, the thickness of the peat deposits start to decrease. Since the 2$^{nd}$ order stream channel, tributary 5, has incised down into the marine sediments, near the channel the mineral sediments are generally within 35-50 cm of the ground surface, however, by about ~ 83 m distance from the stream the depth of organic matter accumulation overlying the sediments increases to about 70-80 cm, and within ~ 400 m from the stream the peat thickens to > 2 m. For the purpose of this study the riparian area is considered to start where the peat begins to thin and there is a break in slope, approximately ~400m from the channel. The geomorphology within the transition from the fen to the channel is complex and distinct from that of the fen (Figure 2-1). Near to the stream there are depressions with pooled water. These depressions are typically several meters removed from the channel and divided from tributary 5 by small levees. The shape of the depressions can vary widely, with some linear and parallel to the stream, which appear to be relic cut-off channels. Others are irregularly shaped and are set back farther from the channel.

The changes in geomorphology, hydrology, and substrate near the stream are associated with differences in vegetation, compared to the dominantly sedge and stunted tamarack cover of the fen. The riparian area is a mixture of forest, dense thicket and mixed riparian swamp similar to that described by Riley (2011). Wetter areas and depressions are covered by dense shrubs > 2 m high including *Alnus rugosa*, *Populus tremuloides*, willow (*Salix spp.*), sedges (*Carex spp.*) and grasses (*Calamagrostis Canadensis*). The better-drained areas have a mixed cover including *Picea mariana* and *Larix laricina*, particularly in the transition from the fen, as well as some other species including *Picea glauca*, *Abies balsamea*, *Alnus rugosa*, and *Populus tremuloides* (Sims, R. 2013).

Soil pipes and small, incised rivulets visually mark locations of surface hydrological connectivity to the stream channel. Six soil pipes were observed along the ~ 1 km section of fen-stream transition. The soil pipes had outlets in the near-stream zone 1-2 meters inland from the stream, and elevated 50 cm to 1 m above the water level of the stream under low (summer) flows. During high (spring and autumn) flows the stream level typically rises above the level of the outlets. The soil pipes have 10-35 cm diameter outlets, which are located at the contact between the organic horizon and the underlying marine sediments. Two soil pipes, denoted pipe A and pipe B, were monitored intensively during this study (Figure 2-1). The outlet of pipe A is upstream of pipe B and the stream is incised to the degree that the elevation of the outlet of Pipe A is 60 cm above the outlet of pipe B, and is located in sediments of a different texture.

In addition to the soil pipes there is surface flow in small, incised channels (~20-50 cm of incision), or rivulets, that flow from the fen to tributary 5. These range in size from ~30 cm to over 1 m in width. Under high-flow conditions the rivulets are easily traced to their origin in the fen, where pools of standing water coalesce to form semi-channelized flow;

however, the channels do not become noticeably incised until they are partially within the riparian area. Four rivulets were identified within the study area, and the most accessible one was selected for intensive monitoring (Figure 2-1). This rivulet was of intermediate size (~50-60cm wide), incised down to the mineral sediments and proximal to pipes A and B.

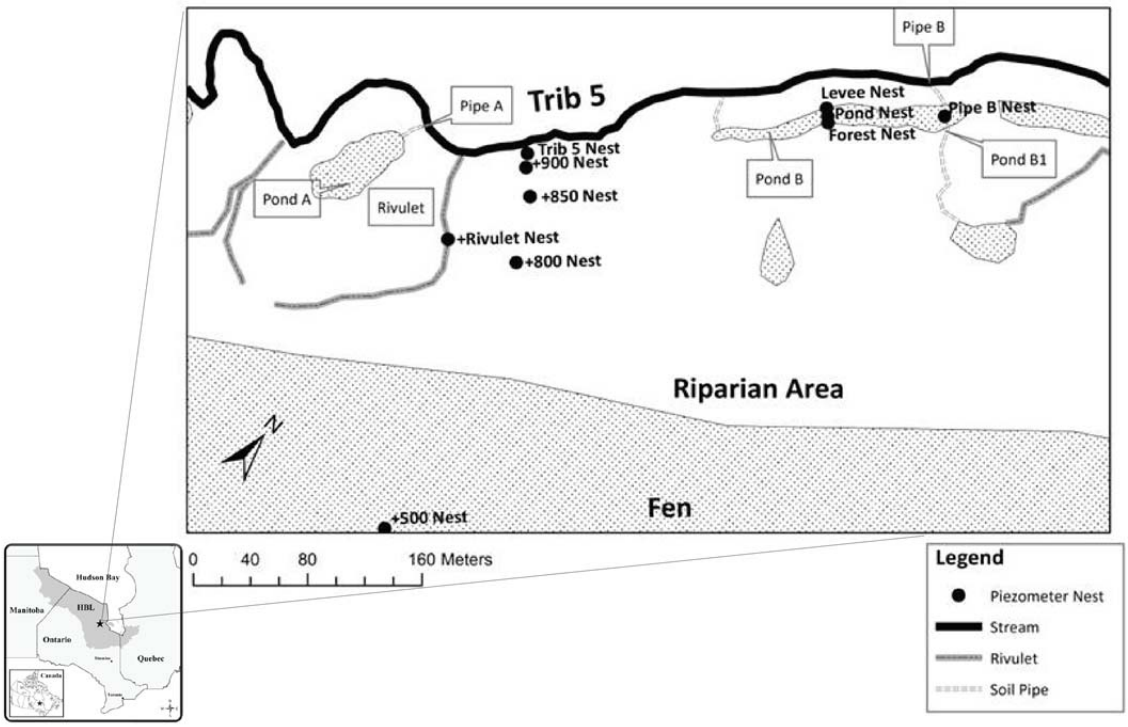


**Figure 2-1: Site Map indicating location of piezometer nests and surface water sampling locations in the riparian area**

## 2.3 Methods

### 2.3.1 Hydrology Measurements: Timing and Magnitude of Runoff and Storage-discharge Relationships

#### 2.3.1.1 Precipitation

Precipitation data was provided by the Ontario Ministry of Environment. It was recorded at half-hourly intervals with a tipping bucket rain gauge located on the ground, and protected with a shield at a meteorological station located in the study fen, approximately 1 km from the riparian study site.

#### 2.3.1.2 Water Table and Groundwater Measurements

A network of shallow piezometers and water table wells were used to monitor shallow groundwater flow directions in the riparian area (Figure 2-1). This network included a transect of 5 nests from the fen to the stream, and transects running perpendicular and parallel to the near stream depression. Additional piezometers and wells were also monitored in the fen.

Piezometers and wells were made from schedule 40 PVC pipe with 30 cm perforated sampling intervals for the piezometers, and perforations along the entire length for the water table monitoring wells. The perforated intervals were screened with 250 μm Nitex® mesh. Piezometers were installed using hand augers, and sediment descriptions were logged at approximately 10 cm intervals during installation. Piezometer depths in the fen ranged from 50-200 cm, installed within the peat and 30-150 cm in the riparian area, with shallow piezometers in the organic horizon, and deep piezometers installed into the mineral sediments. The piezometers installed into the sediments were packed with coarse silica sand and sealed with bentonite in order to prevent leakage down from the overlying organic horizon. The elevation of the tops of the wells and piezometers was measured using a Topcon® (Tokyo, Japan) HiPER GL RTK differential global positioning system (DGPS) with a horizontal accuracy of +/- 1 cm and vertical accuracy of +/- 0.3 cm. These measurements were taken relative to a benchmarked base station in the nearby domed bog. The measurements reflect elevation above the UTM Zone 17N NAD83 Datum and are expressed in meters above sea level.

In the riparian area a nest consists at minimum of a water table well, shallow piezometer installed into the organic horizon and a deep piezometer installed into the mineral sediments. Manual water level measurements were taken on roughly a weekly basis using a 1.5 m long, 0.013 m O.D. PVC tube with a tape measure attached to the outside and lined with Tygon® tubing with the flexible end extending from the top so it can be blown through to detect bubbling at the depth of the water in the piezometer (measurement error ± 0.5 cm). The distance from the top of the well to the ground surface was also recorded. Selected water table wells had hourly water levels recorded by barometrically-corrected submersible pressure transducers (Schlumberger Micro-Divers®) with a resolution of ±2 mm. Water levels were recorded hourly in tributary 5 and the fen, and half-hourly in a near stream depression.

#### 2.3.1.3 Discharge Measurements from Soil Pipes and the Rivulet

Fluxes of water from the soil pipes were measured using v-notch weir boxes (100 cm x 50 cm x 40 cm) made from 18 mm thick plywood. Weir boxes were installed where there was a natural drop in elevation to allow water to fall freely on the far side. They were then leveled to prevent water movement in the box upstream of the v-notch and secured and supported with rebar. The weirs used 27˚ notches in order to maximize the sensitivity of low flow measurements. The weirs were manually calibrated with graduated cylinders and a stopwatch under a range of flow conditions to ensure reasonable agreement with the theoretical relationship between water level in the V-notch and discharge from the weir (Shen, 1981). The weirs were fitted with submersible barometrically-corrected pressure transducers (Schlumberger Micro-Divers®) that recorded water levels at 10 minute intervals. The elevations of the outlets of the soil pipes were also measured using the DGPS.

Discharge in the rivulet was measured using a rectangular flume (100 cm across and 50 cm high) with a frontwall (1.5 m wide) installed into the banks and a bottom lip installed into the bed to ensure all the flow was directed through the flume. The flume was levelled and made flush with the streambed. Manual velocity measurements were taken using a SonTek Flowtracker under the range of flow conditions observed during the fall monitoring period and a stage-discharge relationship developed.

The hydrologic data obtained from water table and flow monitoring was used to determine timing and magnitude of runoff and to explore discharge-storage relationships. For this analysis only storm events that produced measureable and sustained changes in discharge separated by a return to baseflow conditions were selected. This resulted in the inclusion of four multiple-day storm events with rainfall >15 mm.

### 2.3.2 Riparian Zone Hydrochemistry

#### 2.3.2.1 Water Chemistry Sampling

Samples were collected from precipitation, surface water and groundwater from the fen, water from pools and the organic horizon in the riparian area, and shallow groundwater from the sediments in the riparian area. Water samples were collected from the fen wells on a weekly basis to be analyzed for major ions, DOC, and water isotopes. Piezometers in the riparian area were sampled for these species three times, in August (dry), September (intermediate) and October (wet). Flows from the rivulet and soil pipes were sampled weekly, with higher intensity sampling during some storm events dependent on helicopter availability and safe flying conditions. Samples from the shallow groundwater in the sediments and fen were obtained using a peristaltic pump with Teflon tubing to collect water from piezometers, wells, and from shallow pore waters. Samples were taken with a sipper into pre-cleaned, sterile 250 mL PETG sample bottles, which were environmentalized three times by partially filling the bottles with the water intended to be sampled, shaking vigorously and dumping it out, prior to filling the bottle with sample. In the laboratory, the field sample was split for a range of different analyses. Samples for oxygen and hydrogen isotope analyses were stored in 20 ml polyethylene scintillation vials with displacement caps and were checked for air bubbles. Isotope samples from precipitation were collected from a manual rain gauge using well-sealed containers fitted with funnels. Samples from rain gauges were also collected on a weekly basis. Ion samples from precipitation were obtained using a large Teflon funnel taken outside during storm events and collected into a sample bottle before being filtered. Field duplicates and blanks were collected regularly for QA/QC.

#### 2.3.2.2 Chemical and Isotopic Analysis

Ion samples were analyzed using Ion Chromatography on a Dionex ICS-3000 for anions and Dionex ICS-1600 for cations in the Biotron Analytical Services Laboratory at the University of Western Ontario. Analytical blanks were consistently below quantification limits. Duplicates were within allowable limits (20%) with the exception of a small number of samples for species that were very close to the minimum detection limit in concentration. Isotope samples were run on a Picarro L2120 using Cavity Ring-Down Spectroscopy, which has precision of +/- < 0.6 ‰ (δD) and < 0.2 ‰ (δ18O), and are reported relative to the Vienna-Standard Mean Ocean Water (VSMOW) standard.

#### 2.3.2.3 Mixing Model

An end member mixing model (EMMA) was attempted following the general approach of Christopherson and Hooper (1992). In order to maintain consistency with the approach of Orlova and Branfireun (2014), the same conservative tracers (SC, $\delta O^{18}$, $\delta H^2$, $Mg^{2+}$, and $Cl^-$) were used. However, DOC was excluded due to the non-conservative behavior expected over the growing season as DOC was produced in the fen and riparian areas. A Principle Component Analysis (PCA) was performed on the analyzed data to reduce the dimensionality and identify which tracers accounted for the majority of the variation. Vertical hydraulic gradients and chemical gradients for these tracers were analyzed to determine the directions of water movement and potential influence of flow on chemical concentrations in the contributing source areas.

The PCA to determine the number of end members was performed on the rivulet and pipe samples grouped together as well as individually. Bivariate plots were used to determine if the median concentrations of the predicted end members bound the pipe and rivulet data for all combinations of tracers (Hooper *et al.*, 1990) and to test a key assumption of EMMA: that the variability within a single soil horizon is less than the variability between different horizons and also less than the variations in composition of the streamwater. If this requirement is not met, the end members do not satisfy the assumptions of the model (Christopherson and Hooper, 1992).

## 2.4 Results

### 2.4.1 Timing and Magnitude of Surface and Near Surface Runoff

#### 2.4.1.1 Antecedent Water Table and Rainfall for Four Runoff Generating Storm Events

Storm 1 occurred in early August, delivered 15.7 mm of rainfall, and had low antecedent water table elevation: 89.89 meters above sea level (masl.) in the fen, and 87.61 masl. in the near stream depression (Pond Nest on Figure 2-1). These were dry conditions among the storms monitored. Storm 2 occurred later in August, and delivered 33.5 mm of rain, the conditions for this storm were also dry, with an antecedent water table elevation in the fen of 89.89 masl., and in the near stream depression 87.61 masl. Storm 3 occurred at the beginning of September under intermediate antecedent conditions, and had the greatest quantity of rainfall (61.2 mm) observed during the monitoring period. The antecedent water table position in the near stream depression was 87.63 masl., and in the fen 89.93 masl. Storm 4 occurred near the beginning of October and had the wettest antecedent conditions. This storm event produced 37.4 mm of rain, and was preceded by water table elevation in the fen of 90.03 masl., and 87.77 masl. in the near stream depression. In general the runoff from the soil pipes and rivulet was dominated by storm events in the mid to late fall when antecedent water tables were higher (Figure 2-2). By contrast, earlier storms show much more muted responses to rainfall. However, the specifics of runoff response varied among the flowpaths.

During all storm events water table levels rose more quickly in the near stream depression than the fen. However, the length of the lag between peak water table elevation in the fen and peak water table elevation in the near stream depression varied widely among storm events. Under wetter conditions, the lag between the peak elevation in the fen and near stream depression was greater. The fen lagged behind the near stream depression during storm 1 by nearly 5.0 hours, storm 2 by 1.0 h, storm 3 by 52.0 h, and storm 4 by 33.0 h.

The fluctuations in water table were also of higher magnitude in the near stream depression than in the fen. The difference in hydrologic responsiveness between the near stream depression and the fen became most pronounced when conditions were wetter. For example, while the water table in the fen changed by ~10 cm for both storms 2 and 3, the water table in the depression changed by ~10 cm for storm #2 and ~25 cm for storm 3. Subsequent to storm 3, the water table in the fen receded at a gentler slope than it did during storms 1 and 2, however, the water level in the depression receded sharply over the same time period. Due to the difference in the steepness of the water table recessions between the fen and the near stream depression, the highest peak water table in the depression was reached during storm 3, while the highest peak water table in the fen was reached during storm 4.

In general, the riparian area had lower water tables than the fen, however, the presence of near stream depressions increased the variability in local water table elevation. In the fen, the water table was near or above the ground surface (ranging from ~9 cm below to ~15 cm above). In contrast, over the same period of time the water table in the levee nest (situated between a depression and the channel) ranged from ~80 cm below to ~36 cm below ground surface. At a near-stream nest located farther from near stream depressions there were higher water tables adjacent to the channel, ranging from ~13 cm below ground to ~1 cm above ground over the same time period.

#### 2.4.1.2 Rivulet and Pipe Runoff Response

Data for storm 1 is missing for the rivulet due to logger malfunction. For storms 2-4 the measured peak discharge increased from 2.6 to 16.4 l/s, with the greatest increase occurring between storms 2 and 3 (from 2.6 to 7.3 l/s) (Figure 2-2). The time to response decreased as conditions got wetter, from 38.0 hours during storm 2, to < 1 hr during storm 4. The time to reach the peak increased from 51.5 h to 158.5 h between storms 2-4, however, during storm 3 the flow plateaued after 47.0 h but did not reach its peak flow until 156.0 h had passed. The time it took to return to baseflow increased from 128.0 h to 424.0 h between storms 2 and 3, and is unknown for storm 4 because the water level in the rivulet had not returned to baseflow yet at the end of the monitoring period, which unfortunately could not be extended at that point for logistical reasons.

For pipe A, only peak flows for storms 1 and 2 are considered reliable. During storms 3 and 4 the level of tributary 5 rose sufficiently to flood the weir box installed at its outlet, making the readings under peak flow conditions unreliable. Peak flow for storm 1 was 0.2 l/s, and for storm 2 it was 0.3 l/s. However, the time to response was delayed, from 3.0 h to 34.0 h, respectively, and the times required once the response was initiated to reach the peak were delayed 5.0 h and 69.5 h, respectively.

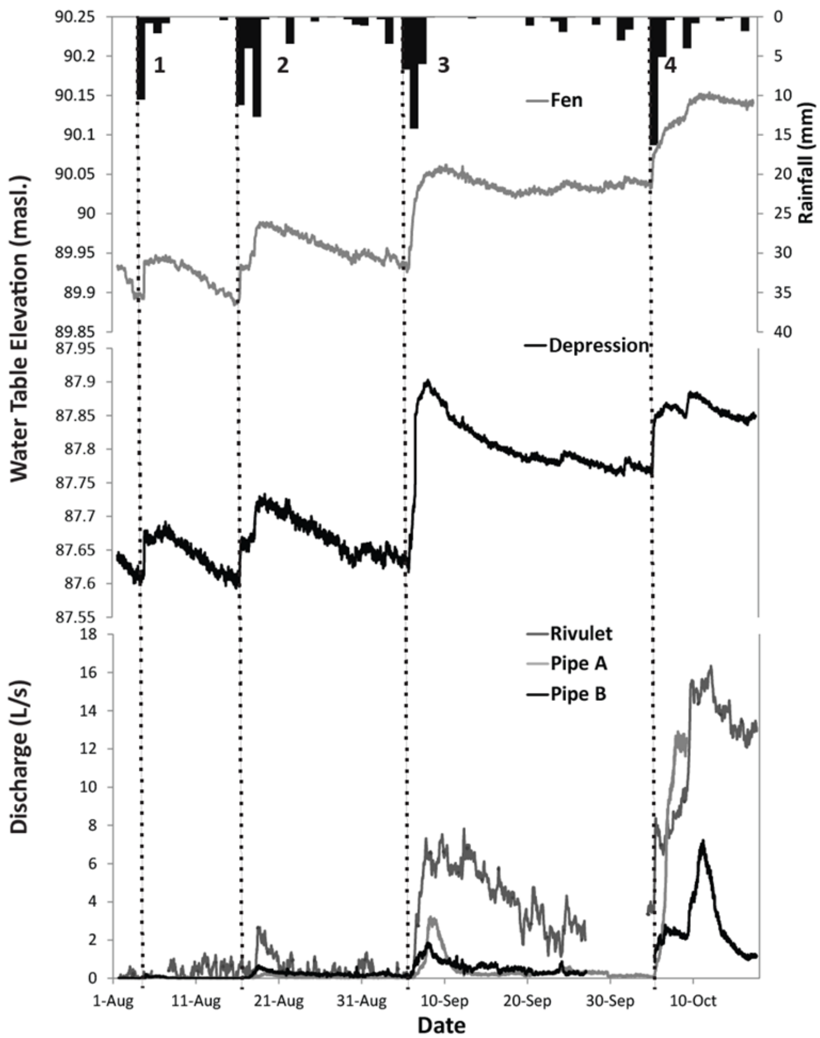


**Figure 2-2: Hydrographs of soil pipes and rivulet with groundwater levels in fen and near stream depression and rainfall plotted above on matching time scale. The four main storm events that are considered in this study are numbered.**

Peak discharges from pipe B were 0.2, 0.6, 1.9, and 7.2 l/s for storms 1, 2, 3 and 4, respectively (Figure 2-2). Therefore, the greatest increase in peak flow (3.8x) was between storms 3 and 4, this is despite storm 3 having nearly 1.6x the quantity of rainfall as storm 4. Furthermore storm 4 had 12x the peak flow of storm 2 despite only having 4 mm more rainfall. The longest time to response was storm 2, which took 28.0 h. For all other storm events the time to response was approximately three hours. Storm 4 may have been slightly quicker, but some of the record is missing. Time to peak and time to return to baseflow was more variable; 5.0, 52.5, 50.5, and 143.5 h and 64.0, 156.5, 168.0, and 264.0 h for Storms 1-4, respectively.

### 2.4.2 Storage- Discharge Relationships

#### 2.4.2.1 Rivulet Discharge and Fen Water Table

The storage-discharge relationship between the fen and the rivulet changed between storms 2 and 3. During storm 2 (dry conditions) there is counterclockwise hysteresis between the fen and the rivulet. At the beginning of storm 2 the water table rose from 89.89 masl. to 89.93 masl. elevation and then plateaued for 28.0 h, before rising again to peak at 89.99 masl. During the initial water table rise the discharge increased from 0.6 to 1.1 l/s, and when the water table plateaued the discharge declined rapidly back to pre-event levels. The later part of the storm showed the discharge rising more quickly relative to the water table (to 2.6 l/s) than it did earlier in the storm. The slope appears to have changed when the elevation of the water table was between 89.96 masl. and 89.98 masl. (Figure 2-3). However, discharge volume still peaked before water table level.

In storm 3, discharge started to increase once the water table reached ~89.96 masl. This threshold was reached earlier in storm 3, and there was little hysteresis between the water table level and discharge. However, once the water table dropped to approximately 90.03 masl. it remained constant while the discharge continued to decrease from approximately 5.5 l/s to 2.5 l/s. Although the record for storm 4 is incomplete, the available record roughly matched the behaviour of storm 3. In storm 4, the antecedent water table was already above the threshold of ~89.96 masl., and the rivulet's response was immediate.

#### 2.4.2.2 Soil Pipe Discharge – Water Table Relationships

The relationship between discharge from pipe A and the water table in the fen changed between the two dry storm events at the start of the season once water tables reached ~89.96 masl. in storm 2. There was little evidence of a relationship between pipe A discharge and the fen water table during storm 1 since the entire rise and fall in discharge occurred during the rise in the fen water table (Figure 2-3). The early part of storm 2 had similar hydrologic behaviour to storm 1. By contrast, once the water table reached the

~89.96 masl. threshold, there was no hysteresis between pipe A and the fen. This was approximately the same threshold observed for generating greater runoff in the rivulet, and for the partial record from pipe A Storm 3.

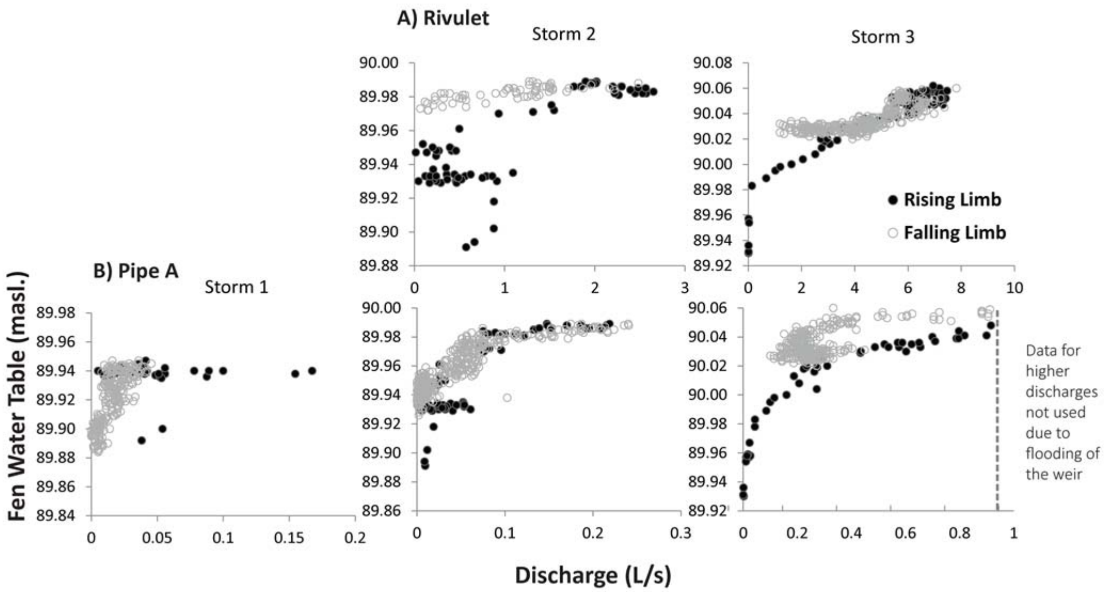


**Figure 2-3: Discharge for the rivulet (A) and pipe A (B) plotted against water table elevation in the fen during storms 1, 2&3. For the rivulet this illustrates the change in slope later in storm 2 as well as the minimal hysteresis apparent in storm 3. Due to logger malfunction, discharge data for the rivulet is missing during storm 1, and the record for storm 3 for pipe A is incomplete.**

The relationships between discharge from pipe B and the water table elevation in both the fen and the near stream depression changed as conditions became wetter between storm 2 and storm 4 (Figure 2-4). During storm 2 there was counterclockwise hysteresis between pipe B discharge and both the near stream depression and fen water tables. When the water table was between 87.65 masl. and 87.67 masl. the slope between pipe B and the depression water table became less steep. In storm 3, the depression water table was already between ~87.65 masl. - 87.67 masl. prior to the storm so the response was immediate and there was no hysteresis in the water table-discharge relationship. During Storm 4 pipe B displays clockwise hysteresis with the near stream depression. During storms 3 and 4 there continued to be counterclockwise hysteresis between pipe B and the fen. Even though the record was incomplete for pipe A it is clear that the patterns of water table-discharge hysteresis with the fen differed between pipe B and pipe A, though they are separated by only a couple hundred meters, since no hysteresis with the fen was documented for pipe A during storm 2.

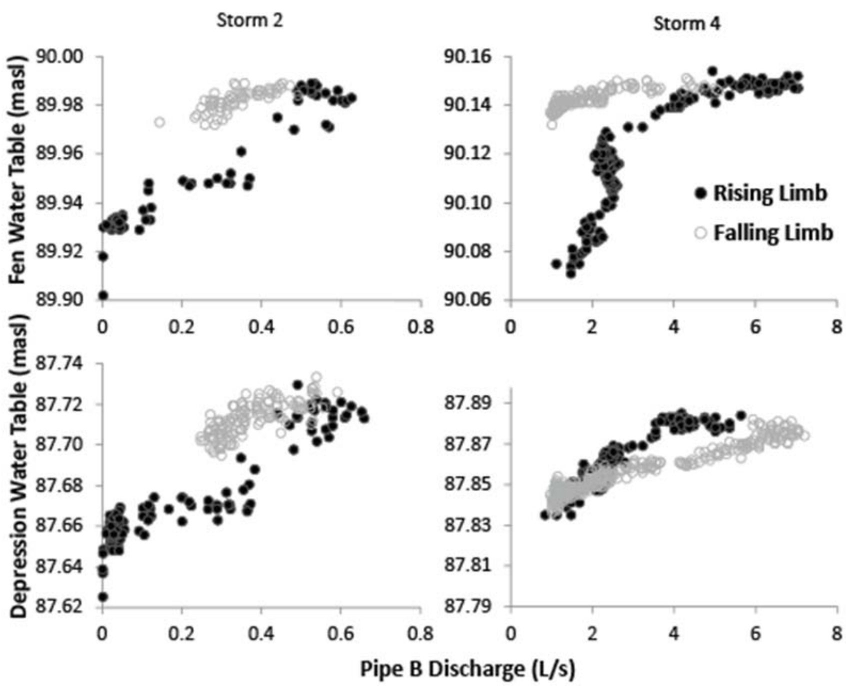


**Figure 2-4: Pipe B discharge-storage relationships with both the fen and the near-stream depression during storms 2 and 4.**

### 2.4.3 Riparian Gradients, Hydrochemistry and Bivariate Mixing Diagrams

#### 2.4.3.1 Hydraulic and Chemical Gradients in the Riparian Area

The strongest vertical hydraulic gradients in the riparian area were measured at the forest nest where the direction of the gradients changed with depth (Figure 2-5). The average gradient over the season from the shallow piezometer to the water table, the 100 cm piezometer to the shallow piezometer, and the 150 cm piezometer to the 100 cm piezometer were 0.4, 0.06, and -0.3, respectively. In the depression, the vertical gradients were weaker and mostly negative with an average gradient of -0.06, between the deep and the shallow piezometers, and -0.03 between the shallow piezometer and the water table. The pipe B nest showed weaker, less negative gradients than the pond nest, with a mean gradient for the shallow and deep piezometers of 0.08 and -0.06, respectively. The gradient in the levee nest was also downwards and weaker. The water table wells in the near stream depression transect running parallel to the longitudinal axes of the depression, consistently showed the highest water table elevations in the middle, which dropped off in either direction towards the soil pipes at either end of the depression.

In general the hydraulic gradients were more positive with proximity to the stream. Fen +900 nest had weak positive average gradients of 0.02 and 0.01. At the fen +800 nest the average gradients were all negative and range from -0.08 to -0.02. These gradients are in a similar range to the average gradients observed in fen +500, with the exception of a positive gradient of 0.04 observed between the 150 and 100 cm piezometers in the fen.

Figure 2-6 depicts chemical gradients for $Mg^{2+}$ and $Cl^-$ at four different locations within the riparian area (refer to Figure 2-1 for locations). The two tracers have different concentration trends. With the exception of the levee nest, $Mg^{2+}$ increased gradually with depth. For example on 29 September: in the depression nest the concentration of $Mg^{2+}$ increased from 1.38 meq in the organic horizon to 1.98 meq in the sediments at 150 cm depth. The levee nest had a steeper gradient between the peat piezometer (with a concentration of 0.07 meq) and the 150 cm piezometer (with a concentration of 2.80 meq). By contrast, the chemical gradients for $Cl^-$ are more variable among sites. At the transition site (+800 nest), concentrations are generally low at all depths (0.01-0.06 meq) except for one sample (0.77 meq). Approximately 120 m away, in the forest nest the concentration in the shallow, 100cm, and 150cm piezometers are 0.43 meq, 10.80 meq, and 9.30 meq, respectively. In the depression nest the concentration in the peat is 0.39 meq, and in the sediments it is 13.90 meq. However, in the levee nest, only 6 m away, the concentration in the peat is only 0.01 meq, while in the underlying mineral sediments it is 2.76 meq.

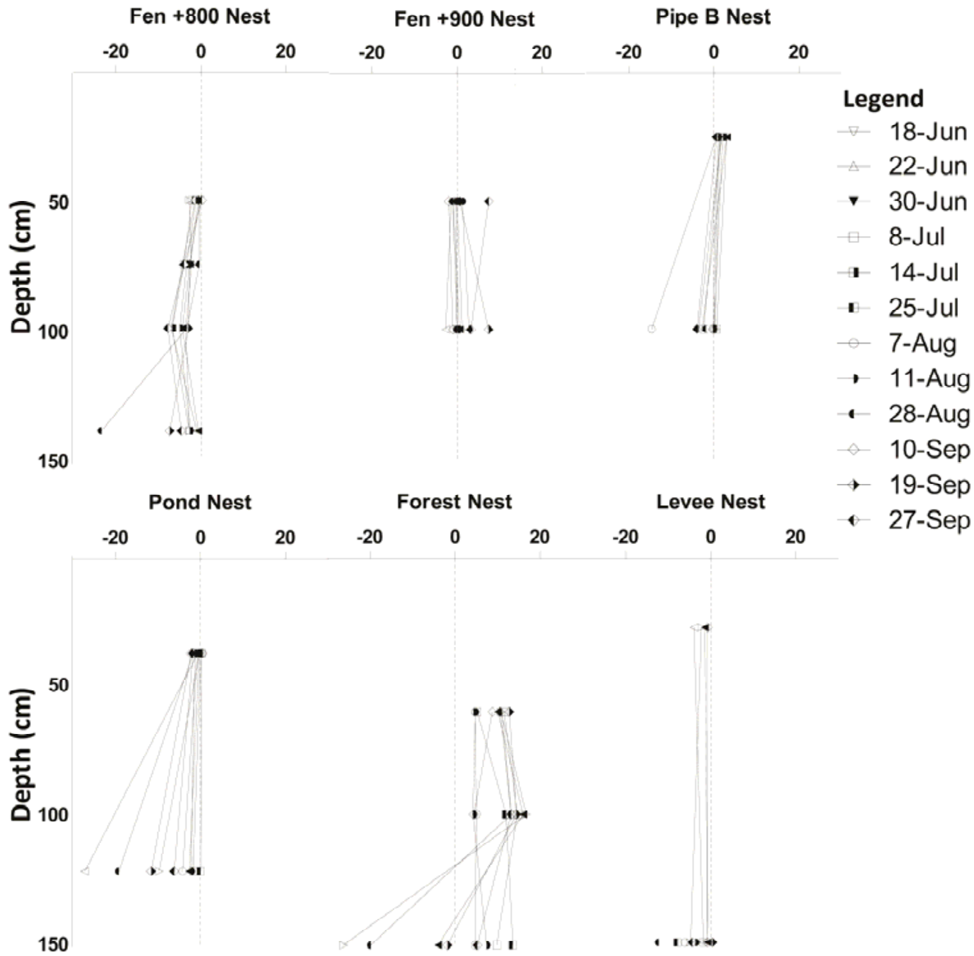


**Figure 2-5: Hydraulic gradients at different times in the riparian area at a subset of the piezometer nests. Gradients are calculated with respect to water table, with a positive gradient indicating upward flow and the steepness of the gradient also reflected by the slope of the line. At the Forest Nest, the 100 cm piezometer is installed into a lense of coarser sediments within much more cohesive and fine grained material, this lens disappears between the Forest Nest and the Pond Nest which is next in the transect, this may explain the diversion of flow suggested by the diverging gradients from this depth.**

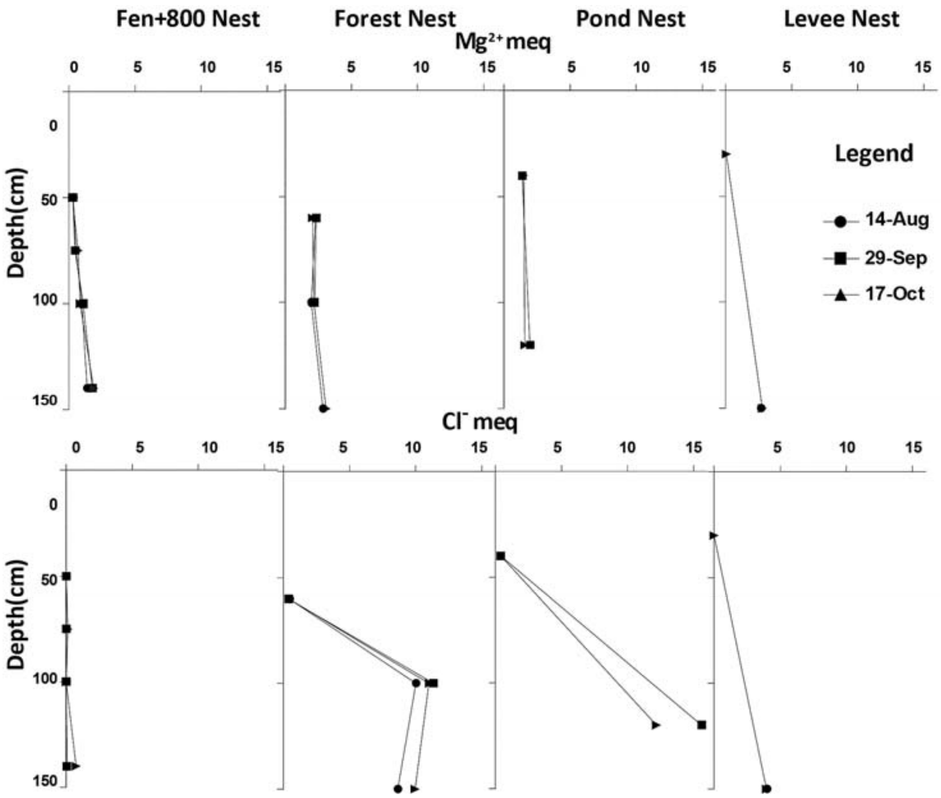


**Figure 2-6: Chemical gradients over time in the riparian area at a subset of piezometer nests for $Mg^{2+}$ and $Cl^{-}$.**

## 2.4.3.2 Bivariate Mixing Diagrams

The shallow groundwater concentrations for $Mg^{2+}$ ranged from 0.47 meq to 3.50 meq, while $Cl^{-}$ concentrations ranged from 0.01 to 15.60 meq. Organic horizon concentrations of $Mg^{2+}$ ranged from 0.07- 2.77meq, and $Cl^{-}$ concentrations from 0.01 to 3.75 meq. By contrast, between August and October pipe A, pipe B, and the rivulet ranged in concentration from 0.18-0.38 meq, 0.24-0.43 meq, and 0.18-0.71 meq, respectively for $Mg^{2+}$, and 0.03-0.16 meq, 0.07-0.14, and 0.01 to 0.04 meq, respectively for $Cl^{-}$. Due to the wide variety in concentration for the riparian potential source waters (organic horizon and shallow groundwater) they are depicted on the bivariate plots in two groupings based on the clustering of the individual samples in the bivariate mixing space; GW/OH Group 1 which consisted mostly of samples collected near the near stream depression, and GW/OH Group 2 which consisted mainly of samples collected along the main transect from the fen to the stream. The distinction between the two groupings was particularly stark when $Cl^{-}$ was used as a tracer.

The PCA identified two principal components (that correlated strongly with $Mg^{2+}$/SC and $\delta O^{18}$) with eigenvalues greater than 1. Within the $Mg^{2+}$ and $\delta O^{18}$ mixing space, the rivulet and pipe A partially overlapped, while pipe B was completely distinct due to its depleted $\delta O^{18}$ isotope signature (Figure 2-7). Pipe B plotted closer to pond B, pond B1 and some of the organic horizon samples from the GW/OH Group 1 while pipe A and the rivulet both plotted between the shallow fen and a cluster that includes the deep fen and some of the GW/OH Group 2 samples. Both pipe A and the rivulet plotted closer to the fen samples (shallow and deep) than the samples from pipe B did.

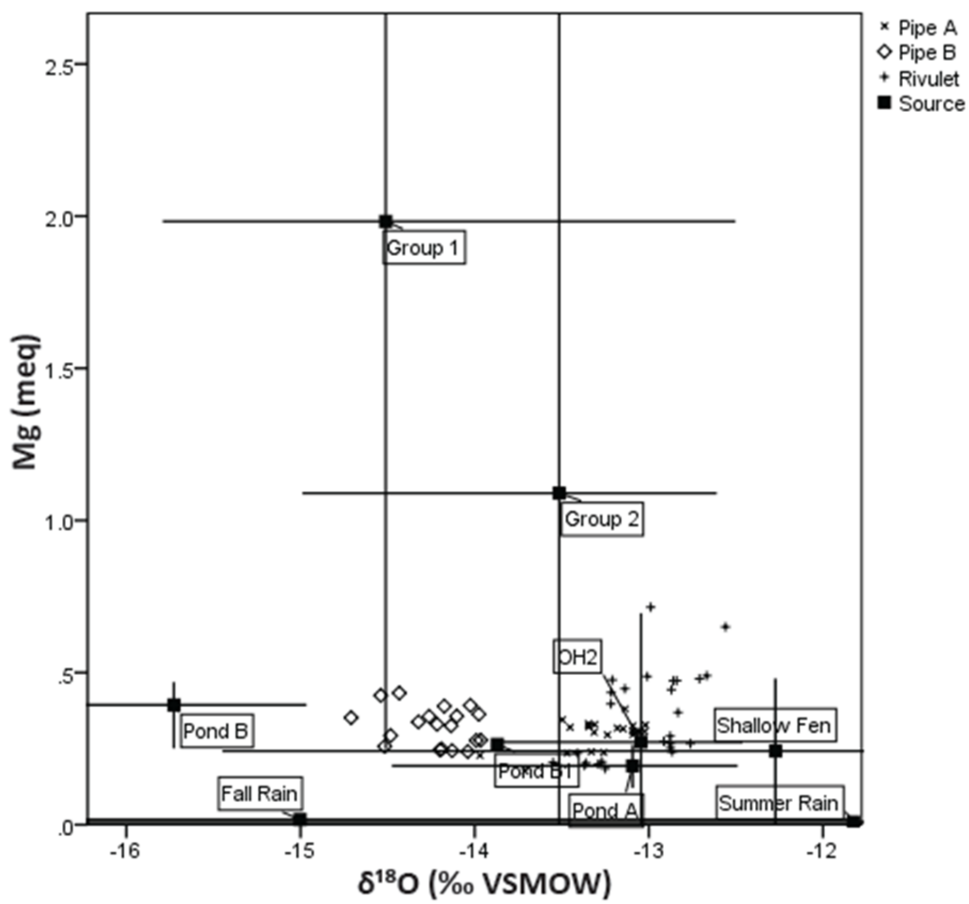


**Figure 2-7: Bivariate mixing space for $Mg^{2+}$ and $\delta O^{18}$, tracers identified by the PCA. For the potential sources, the squares indicate the median concentrations, while the error bars represent the range of concentrations observed for the different samples in that category. Group 1 and Group 2 refer to the median values of the 2 clusters of**

**shallow groundwater and organic horizon samples as discussed above, the organic horizon samples corresponding to Group 2 groundwater, plotted separately and closer to the fen in this mixing space, as shown by OH2.**

Since the chemical gradients for $Mg^{2+}$ were different than for $Cl^-$, the bivariate plot for these two tracers was also included for comparison. In the bivariate plot for $Mg^{2+}$ and $Cl^-$ the concentrations for pipe B and pipe A generally overlapped (Figure 2-8). Even though the concentrations were similar for both soil pipes there was a difference in the seasonal pattern. In both soil pipes, the concentrations of both solutes generally increased together, however, $Mg^{2+}$ and $Cl^-$ did not peak at the same time for pipe A, though they did for pipe B. At the end of the summer pipe A had higher $Cl^-$ than pipe B (0.15 meq, compared to 0.13 meq), but concentrations in pipe A decreased more rapidly following storms 2 and 3 resulting in pipe A having a concentration of 0.05 meq, while pipe B still had a concentration of 0.12 meq in late September. By the end of storm 4 the concentration in pipe B (0.07meq) was still approximately double that of pipe A (0.03meq). By contrast, the concentrations of $Mg^{2+}$ were more constant for both pipe A and pipe B, maintaining concentrations of approximately ~0.30 meq, until storm 4 where concentrations dropped down to approximately ~0.20-0.25 meq for both.

The rivulet could be clearly distinguished from the soil pipes by its lower $Cl^-$ concentration. In the summer, the rivulet samples had higher concentrations of $Mg^{2+}$ than the soil pipes (average = 0.36 meq, and max of 0.71 meq) and plotted closer to the deep fen and GW/OH Group 2 samples. The seasonal trend for concentration of $Cl^-$ in the rivulet was opposite to that of the soil pipes. As the $Mg^{2+}$ concentrations decreased, the concentration of $Cl^-$ increased over the fall season, from 0.01 meq in August to a maximum of 0.04 meq. The highest concentrations of $Cl^-$ in the rivulet occurred during the largest storm at the end of the fall, which was when the lowest concentrations occur in the soil pipes. Within the mixing space both the rivulet and the soil pipes converge towards the shallow fen as conditions get wetter.

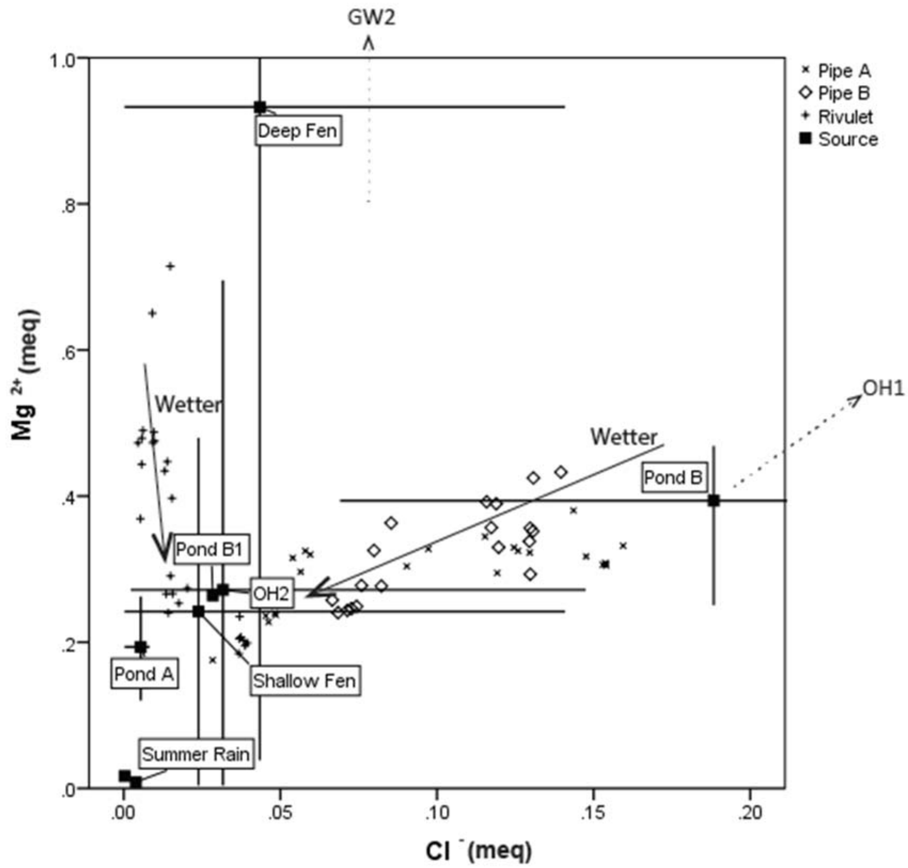


**Figure 2-8: Bivariate mixing space for $Mg^{2+}$ and $Cl^{-}$, showing only the subset of potential sources that plot close to the mixing space for the soil pipes and rivulet, arrows indicate direction in which the groundwater samples from group 2 (GW2) and the organic horizon samples from group 1 (OH1) would plot that are too far from the mixing space to include, as well as the trends towards the wetter part of the monitoring season.**

## 2.5 Discussion

### 2.5.1 Timing and Magnitude of Event Response

Antecedent water table elevation in the fen and near stream depression had a strong influence on runoff generation in soil pipes and rivulets, but the relationships varied among flowpaths. This variability reflected the ability of near stream depressions to provide storage and generate runoff, delaying connection with the fen for some flowpaths. Thresholds for runoff generation in the near stream depression were met at different times relative to the threshold in the fen, in part because the near stream depression was more hydrologically responsive than the fen. This suggests that peak runoff generation from the riparian area could precede peak runoff generation from the fen.

### 2.5.2 Connectivity and Storage

Near stream depression storage appeared to both delay and limit the connectivity of pipe B to the fen. The rivulet became connected to the fen by mid-September; storm 3, whereas pipe B became partially connected to the fen during storm 4 in early October. At this time the rising limb was still controlled by the near stream depression, but the overall discharge was larger, likely as a result of the fen contributing during the falling limb. The connectivity of the rivulet with the fen, reflected by increased discharge, seemed to be controlled by a fen threshold, whereas increased connection between pipe B and the fen appeared to result from the satisfaction of storage in the near stream depression. The differences in water chemistry support these interpretations of connectivity since the rivulet plots closer to the fen and pipe B plotted closer to riparian pools and shallow groundwater, and organic horizon in the bivariate plots. The nature of connectivity between pipe A and the fen was not as well characterized. This is partially due to the flooding of the weir. However, in the mixing space it plotted closer to the fen than pipe B did and appeared to respond to the same fen water table threshold as the rivulet. The difference in timing and connectivity between pipe A and pipe B indicates spatial variability in the riparian area and suggests that it may be difficult to generalize the nature of fen to channel connectivity even on the scale of a couple hundreds of meters. However, the storage-discharge relationships suggest that connectivity may be threshold mediated in this environment.

The importance of storage thresholds in controlling connectivity and runoff generation has been demonstrated in other environments; especially in bedrock controlled heterogeneous catchments in the Canadian Shield (e.g., Oswald *et al.*, 2011; Phillips *et al.,* 2011; Spence *et al.,* 2010; Spence, 2010). Researchers such as Oswald *et al.* (2011) found that in the Canadian Shield, runoff is related to threshold mediated connectivity between discrete landscape units and these units can have disproportionate importance for runoff generation, especially when in a terminal position. Quinton *et al.* (2003) have already identified the importance of threshold-mediated connectivity for generating runoff in the context of other northern peatlands in the Northwest Territories. Within the HJBL Richardson *et al.* (2012) found that channel fens and fen water tracks close to the stream control catchment efficiency for the tributaries of the Attawapiskat River. Based on our results, we can narrow this zone to the relatively small transitional zone between these near stream fens and the stream channel that act as the final regulator of runoff. We propose that at our study site, terminal storage units within the riparian area may exert a disproportionate control on runoff magnitude and timing. These near stream depressions are hydrologically responsive and once water levels reach threshold levels they can be efficiently drained by flow in soil pipes. This likely contributes to more hydrologically responsive behaviour for tributary 5 than if it was directly controlled by the fen. Storage in the depressions of the riparian area also helps to delay peak flows until later in the fall by attenuating flows from the fen until the near stream depression storage thresholds are met. This heightened efficiency and sensitivity to storage thresholds might make runoff generation in this environment more sensitive to climate change as Carey *et al*. (2010) have proposed in other northern catchments, because small changes to evapotranspiration and precipitation rates could result in large changes to runoff generation.

### 2.5.3 Riparian Hydrochemistry and Mixing

The difference in concentration trends for $Cl^-$ and $Mg^{2+}$ reflect the hydraulic gradients in the near stream depression. In the forest nest, vertical flow diverged at ~100 cm depth, and this depth also had the highest concentration of $Cl^-$. This piezometer was installed into a distinct ~10-20 cm lens of coarser grained sediments, which was not observed when installing in either the depression or the levee. The hydraulic and chemical gradients suggest that $Cl^-$ may be transported in the 100 cm deep layer to the forest, but there the flowpaths diverge resulting in mixing both above and below. This divergence may occur as a consequence of the pinching out of the coarser lens observed at the 100cm depth, the water following this preferential flow pathway may be diverted as it meets more sediments that are potentially less permeable. The high $Cl^-$ concentrations at 150 cm depth in the depression suggests lateral flow from the forest. The similarity of $Cl^-$ concentrations in the organic horizon of both nests likewise suggests lateral flow through the organic horizon. The sediments in the levee nest were more cohesive and finer grained than either the forest or the depression, which seems to have limited lateral flow and mixing, resulting in lower concentrations of $Cl^-$ in the levee organic horizon and sediments relative to the depression or the forest.

The pattern of distribution of $Mg^{2+}$ concentrations is much more homogenous across the site, and changes less dramatically with depth. Unlike $Cl^-$, the patterns of $Mg^{2+}$ do not appear to reflect the hydraulic gradients measured in the riparian area. This suggests that the $Mg^{2+}$ is derived *in situ* while the $Cl^-$ is delivered from groundwater. Orlova and Branfireun (2014) also identified an end member high in $Cl^-$, (as well as $Na^+$ and $SO_4^{2-}$) which they attributed to a deep bedrock source. However, at our study site similar chemistry was encountered in the groundwater from shallow unconsolidated sediments, at less than 2 m depth. The shallow sediments of the riparian area therefore appear to be a mixing zone for at least two ground water sources. This results in variable chemistry within the organic horizon and shallow sediments that made it unrealistic to identify appropriate stable end members for the mixing model.

The concentrations of the tracers varied on a small scale (<10 m horizontally/ <1 m vertically) that made defining organic and shallow ground water end members for use in a mixing model unfeasible, given the spatial resolution of sampling. The degree of variability in the concentrations of the ion tracers ($Mg^{2+}$ and $Cl^-$) within the riparian organic horizon and shallow groundwater samples, which are potential sources of water to the soil pipes/rivulet, was greater than the variability of concentrations in the soil pipes/rivulet with flow. This violated one of the key assumptions of EMMA. Quantifying the end members contributions based on this data was therefore not reasonable, however, bivariate mixing plots were used to identify potential runoff sources within the riparian area. To simplify interpretation, the organic horizon and shallow groundwater samples were divided into groups that roughly reflected their geographic location and chemistry.

There are many examples of environments where the riparian area has a distinct chemical signature from that of the hillslope (eg: Hooper, 1998; Burns *et al.,* 2001; McDonnell and McGlynn, 2004). In some environments the riparian aquifer acts as a conservative mixing space where the dynamics of the mixing zone could be controlled by the relative volumes of hillslope and riparian storage available and by the antecedent water table position (Burns *et al*., 2001). The importance of antecedent water table to hydrochemistry was also observed at our site. As the riparian storage is satisfied and greater connectivity with the fen is achieved later in the fall, the chemistry of the soil pipes and rivulet converges towards the signature of the shallow fen (Figure 2-8). However, the organic horizon and shallow groundwater samples from our study site could not be characterized as conservative mixtures of other stable end members. Mixing has been observed in alluvial aquifers when storage is provided that allows chemical reactions to proceed in the riparian area between storm events (Hooper *et al*., 1998). At our study site both mixing and biogeochemical activity may be occurring as a result of storage provided by near stream depressions, and within the organic horizon.

### 2.5.4 The Riparian Zone as Hydrological Gatekeeper

The hydrological and hydrochemical importance of riparian zones has been well documented in many environments (Vidon *et al.,* 2010). However, in the low gradient, peatland dominated, landscape of the HJBL the riparian areas were not assumed to be analogous to riparian zones in areas with greater topographic relief. Riparian areas adjacent to hillslopes typically have higher water tables, gentler topographic gradients, and greater accumulations of organic matter relative to the hillslope. By contrast the riparian zone in our study had lower water tables, steeper topographic gradients, and less accumulation of organic matter relative to the fen. We found that the riparian area behaves as a gatekeeper between the fen and the stream, in a similar way to riparian zones adjacent to hillslopes. Burt (2005) described the paradoxical role of the riparian area as both a transmitter and a barrier for both flow and biogeochemistry. At our site this paradoxical character is reflected by the partial and spatially variable nature of connectivity between the fen and the stream resulting from the variety of flowpaths within the riparian area. In the HJBL, Riley (2011) defined two separate flow systems, one consisting of the peatlands, and the other consisting of the incised channels. However we argue that, for the headwater streams in this region, there is a connection between these two flow systems mediated by the riparian area.

Based on our results the nature of this connection depends on the antecedent water table levels, and is spatially variable through the riparian area. We propose a conceptual model where the fen and near stream depressions represent 2 different storage elements, the fen element obviously being significantly larger (Figure 2-9). However, because of its terminal position relative to the stream, the near stream depressions can exert a greater control over runoff-response under dry conditions when the broader landscape is disconnected. Since near stream depressions are not continuous along the channel banks the fen experiences differing degrees of connectivity with the stream. Rivulets allow a more direct connection between the fen and the stream, bypassing the riparian area. By contrast, runoff in soil pipes appears to be more closely related to near stream storage elements. Seepage likely occurs in the shallow riparian organic horizon, between the fen and the near stream depressions and directly to the stream, however chemistry samples from the organic horizon suggest mixing with the shallow groundwater in the marine sediments below. The nature of connectivity changed over the season:

1) Under very dry conditions in the late summer flow ceases or decreases to a slight trickle in the soil pipes and rivulets. During the first storm event there did not appear to be a relationship between storage in the fen or near stream depression and runoff, suggesting that bypass flow may drive runoff response under these conditions.
2) Intermediate conditions allow the rivulet to become fully connected to the fen, while soil pipes may become fully connected to the near stream depression. Water levels in the riparian organic horizon become high enough that subsurface flow may also contribute to stormflow.
3) Under wet conditions the rivulet continues to be connected to the fen while some of the soil pipes are still controlled by the more hydrologically responsive near stream depression on the rising limb, but appear to be controlled by the runoff from the fen during the falling limb resulting in higher discharge. This relationship was similar to relationships observed in hillslope-riparian transitions

(e.g. McDonnell *et al*., 1998). This connectivity reflects subsurface flow between the fen and near stream depression driven by the hydrologic gradient. Likely this phase results not only when available storage is satisfied in the near stream depressions, but also when water tables in the riparian area become high enough to allow significant flow through the organic horizon rather than the low permeability marine sediments.

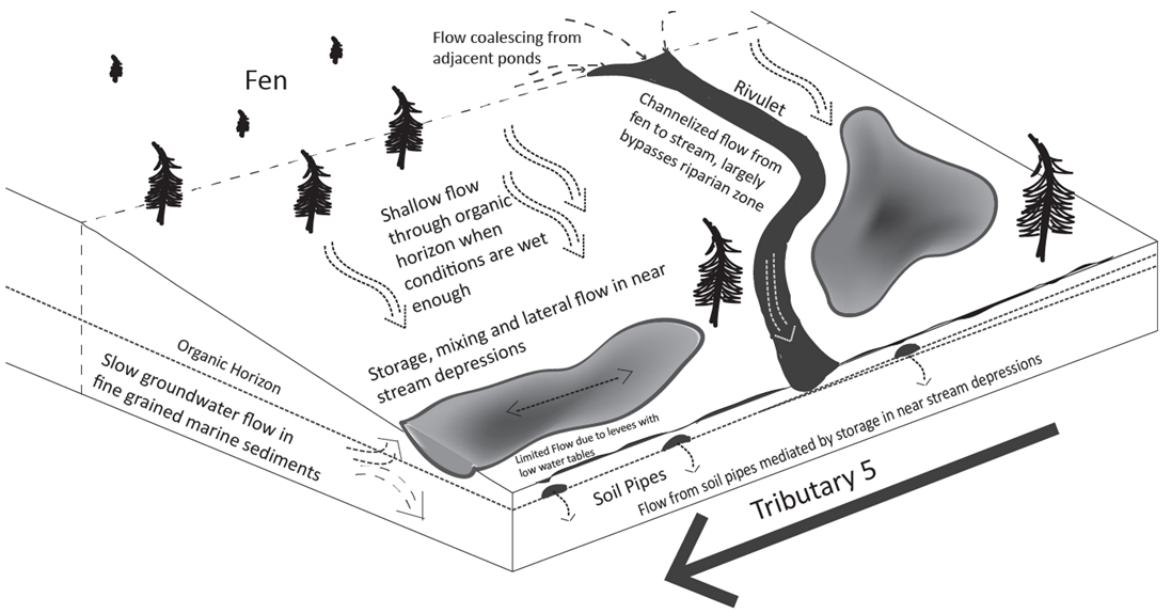


**Figure 2-9: Conceptual Diagram.**

## 2.6 Conclusions

The presence of near stream depression storage, soil pipes, and rivulets that have distinct hydrological behaviour from the fen and from each other suggests that the simple assumption that the fen is connected to the stream by seepage flow through the riparian area governed primarily by changes to water table elevation in the fen, must be questioned. Instead, the riparian area has distinct chemical and hydrological characteristics that moderate the flow of water and solutes from the fen to the stream, and therefore, fulfills a similar role to that of riparian zones in hillslope environments. Our observations suggested that the rivulets allow the flow of water from the fen to largely bypass the riparian area by providing a direct, rapid, connection between the fen and the channel, with minimal mixing. By contrast, the hydrological role of the soil pipes in the riparian area is more complex. They become hydrologically connected in a stepwise fashion as conditions become wetter during the autumn. During mid-autumn storms, with intermediate antecedent water table elevations, soil pipes are primarily connected to riparian depressions adjacent to the channel. Later in the autumn, when storm events occur under wetter conditions, the soil pipes become connected to both the riparian depressions and the fen. The degree of connectivity is mediated by thresholds in antecedent water table level within the riparian area and the fen. Differences in available storage in the riparian zone means that the timing of connectivity varies amongst the soil pipes and rivulets. This suggests that detailed monitoring of the riparian area should be incorporated into any attempt to model or predict runoff in this environment, and that it should be treated as a discrete landscape element relative to the fen, and that runoff generation may be sensitive to relatively small changes in evapotranspiration or precipitation.

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# 3 The Influence of the Riparian Zone on Peatland-Surface Water Mercury and Carbon Export in a Peatland-Dominated Subarctic Catchment

## 3.1 Introduction

Mercury is a global pollutant and toxic element that is hazardous for both humans and wildlife (Fitzgerald and Clarkson, 1991). In many terrestrial and aquatic systems the majority of Hg is associated with dissolved and particulate organic matter, as a result of the strong binding that occurs between Hg and reduced sulfur groups in the organic matter (Schuster, 1991; Driscoll *et al.*, 1995; Kolka *et al.*, 1999; Skyllberg *et al.*, 2000; Grigal, 2003; Ravichandran, 2004). Since the Hg and carbon cycles are intimately linked, the same hydrological pathways commonly control the transport of both Hg and organic carbon from terrestrial to aquatic systems (Kolka, 1996). This means that Hg fluxes in watersheds are often strongly associated with the transport of dissolved and particulate carbon (Kolka *et al.*, 1999; Ravichandran, 2004).

Although the majority of Hg found in water is inorganic Hg(II), the organic Hg species MeHg is of greater ecological concern because it is a potent neurotoxin that bioaccumulates (Rudd, 1995; Ullrich *et al.,* 2001). Since atmospheric sources of MeHg are not sufficient to explain MeHg fluxes from terrestrial watersheds, the majority of MeHg results from the methylation of inorganic Hg in watersheds (St Louis *et al.*, 1994). The Hg methylation process is commonly mediated by sulphate-reducing bacteria (Morel *et al.*, 1998; Ullrich *et al.*, 2001). Conditions that may stimulate this microbial activity include temperature (Ullrich *et al.*, 2001), abundant labile organic matter (e.g. Bodaly *et al.*, 1997), increased inputs of sulphate (Branfireun *et al.*, 1999), and an anaerobic environment (Ullrich *et al.*, 2001).

Wetlands and especially peatlands, have been recognized as playing a pivotal role in MeHg production and export from terrestrial systems. This is because their high water tables help maintain an anaerobic environment and promote the accumulation of organic matter, providing conditions that can facilitate the methylation and transport of Hg (e.g. St Louis *et al.*, 1994; Bishop *et al.*, 1995; Branfireun *et al.*, 1996; Grigal, 2002). Wetland abundance within a watershed is therefore an important determinant of downstream MeHg concentrations (e.g. Brigham *et al.*, 2009). Riparian areas have been identified as an important source of MeHg to streams, as they can have significantly higher concentrations in soils and pore waters than the surrounding uplands (Bishop *et al.*, 1995) As the interface between terrestrial and aquatic ecosystems, riparian zones are often sites of elevated biogeochemical reaction due to mixing and sharp gradients of vegetation, soil type and hydrology (McClain *et al.,* 2003; Vidon *et al.,* 2011).

It has been recognized that short episodes of elevated flow can be disproportionately important to determining total Hg and MeHg flux from the terrestrial landscape (e.g. Bishop *et al.*, 1995; Bushey *et al.*, 2008; Mitchell *et al.,* 2008; Shanley *et al.*, 2008; Demers *et al.*, 2010,). However, the relationship between flow and Hg transport is complex because in some contexts Hg concentrations are decreased by high flow events (dilution), while in others Hg concentrations are elevated during high flow events (flushing) (e.g. Bishop *et al.*, 1995; Branfireun and Roulet, 2002; Bushey *et al.*, 2008; Brigham *et al.*, 2009). Elevated Hg concentrations are often observed during storm events, however this positive relationship between flow and Hg concentration may not be consistent over a season (Schuster *et al.*, 2008; Shanley *et al.*, 2008; Bushey *et al.*, 2008; Brigham *et al.*, 2009; Demers *et al.*, 2010). This suggests the importance of understanding Hg dynamics during storm events for determining overall Hg transport. For example in one agricultural watershed, the entire season's yield of Hg was dominated by a single storm event (Babiarz, 1998). Branfireun *et al.* (1996), working in the Canadian Shield, found that although stormflow only occurred during 16% of the 112 day study period, elevated MeHg concentrations during summer storms meant stormflow accounted for 53% of the MeHg mass flux in a stream. In addition to storm events, elevated flow during snowmelt can be very important for total Hg export from some watersheds. In temperate, peatland-dominated watersheds, Mitchell *et al.* (2008) found that 26-39% of annual Hg flux may occur during a 12 day long snowmelt period. Alternately, other studies have observed dilution effects on MeHg under higher flow conditions (e.g. Bishop *et al.*, 1995; Branfireun and Roulet, 2002). Therefore it is vital to understand the specific event dynamics of total Hg (THg) and MeHg within a given catchment, in order to estimate overall Hg transport.

Catchment characteristics such as hydrological responsiveness, land-cover, vegetation, and geomorphology, influence Hg phase and transport within a watershed (Hurley *et al.,* 1995). The differences between wetland dominated and non-wetland catchments can also influence the partitioning between the dissolved and particulate fractions of Hg (Hurley *et al.,* 1995; Babiarz *et al.*, 1998; Brigham *et al.*, 2009). For catchments with abundant wetlands the dissolved phase is typically most important (Hurley *et al.,* 1995; Babiarz *et al.*, 1995). In forested watersheds, higher Hg concentrations can occur when water table rises because the higher water levels can result in flushing of dissolved Hg from the DOC-rich upper layers of soil (Dittman *et al.*, 2010). By contrast, in forested and agricultural watersheds that are more hydrologically responsive, dramatic fluctuations of Hg concentration with flow can result from the erosion and mobilization of particle-bound Hg to the stream (Babiarz *et al.*, 1995; Lawson and Mason, 2001; Shanley *et al.*, 2002).

Carbon and Hg export from peatlands to aquatic systems are both expected to increase as a result of predicted climate changes such as increased temperature and changing precipitation patterns (Mart, 2007). The HJBL are the second largest peatland expanse on the planet (Riley, 2011), and this northern landscape is expected to be particularly vulnerable to climate change (Gough and Wolfe, 2001). As discussed above, peatlands are often sources of MeHg to downstream aquatic systems, but little is known about Hg and carbon dynamics within this vast peatland-dominated landscape. Although elevated concentrations of MeHg have been observed in young of year fish (Warnock, unpublished data), current data suggests that MeHg in these peatlands, as well as the stream network, are typically very low (often close to quantification limits) (Victor Project unpublished data). Organic matter decomposition and Hg methylation are both biologically mediated processes that respond to temperature (Moore *et al.*, 1998; Ullrich *et al.*, 2001). As a result, DOC and MeHg concentrations may increase during the growing season in wetland-draining streams (Branfireun and Roulet, 2002; Selvendiran *et al.*, 2008). This makes the late summer and early fall potentially important time periods for Hg and carbon export from the fen. Storm events during the late summer and early fall may result in episodes of elevated export of MeHg and DOC, however, to this date the remote nature of this landscape has prevented intensive sampling during storm events for THg, MeHg and DOC. The objectives of this study were to:

1) quantify the fluxes of THg, MeHg and DOC from a fen to a 2nd order stream via surface and shallow subsurface preferential flow pathways through the riparian area during the late summer and early fall (August-October),
2) characterize the storm event concentration dynamics for THg, MeHg and DOC in these flow pathways, and
3) determine the relative importance of the riparian area compared to the fen for THg, MeHg and DOC export to the stream channel.

## 3.2 Site Description

The research site is located at (52.83˚ N, 83.93˚ W) in the Central James Bay Lowland of Northern Ontario within the HJBL. The study site is in the riparian area at the interface between a ~ 6 km long patterned fen and the stream channel (tributary 5) and is described in detail in Chapter 2. Two soil pipes, denoted pipe A and pipe B, and one rivulet were monitored intensively during this study (Figure 3-1).

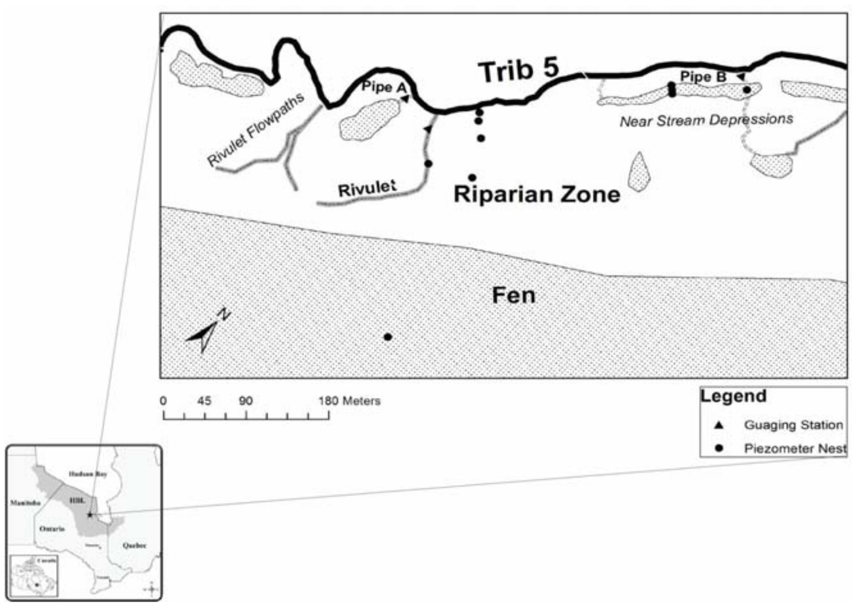


**Figure 3-1: Location of field site in Northern Ontario, inset provides locations of the fen, riparian transition, and sampling locations within the riparian area. Also**

**illustrates the basic geomorphologic features of the riparian area; depressions, rivulets and soil pipes.**

## 3.3 Methods

### 3.3.1 Hydrology measurements

Precipitation and discharge data were collected during the field season of 2012. A continuous record of discharge in soil pipes was measured using v-notch weirs and flow in the rivulet was measured using a rectangular flume. The detailed methodology applied for hydrological measurements such as discharge from soil pipes and rivulet, as well as procedures for piezometer installation and monitoring are described in Chapter 2.

### 3.3.2 Water Chemistry

#### 3.3.2.1 Sampling in the Fen

Samples for DOC and Hg analyses were collected from surface water and groundwater from the fen. During the late summer and fall (July 25-Oct 17), water samples were collected from the fen wells on a weekly basis to be analyzed for DOC and a biweekly basis for filtered total Hg ($THg_{FILT}$) and filtered MeHg ($MeHg_{FILT}$). The data for pore and surface water in the fen was supplemented by data collected by Ulanowski (2014) in 2011.

#### 3.3.2.2 Sampling in the Riparian Area

Water samples for DOC and Hg analyses were collected from surface water in pools and shallow groundwater from the riparian organic horizon, and sediments. Water samples for carbon and Hg analysis were also obtained from soil pipes and rivulets that flow through the riparian area. Pool samples in the near stream depressions were collected weekly for DOC and biweekly for $MeHg_{FILT}$ and $THg_{FILT}$ starting in April and continuing through the summer until the pools dried up. Water samples for DOC analysis, were collected from piezometers in the riparian area three times, in August (dry), September (intermediate) and October (wet). Water levels were too low to obtain sufficient sample volume for $MeHg_{FILT}$ and $THg_{FILT}$ until October in riparian piezometers. Water from rivulets and soil pipes were sampled biweekly for all solutes starting in April. However, more intensive sampling at one of the rivulets and two soil pipes (pipe A and pipe B) was performed weekly between July 25th and October 17th to be analyzed for DOC, $MeHg_{FILT}$, $THg_{FILT,}$ unfiltered MeHg ($MeHg_{UNFILT}$), and unfiltered THg ($THg_{UNFILT}$). Higher intensity sampling (every couple hours if possible, or at least daily) was done during storm events dependent on helicopter availability and safe flying conditions. The data for pore and surface water in the riparian area was supplemented by data collected by Ulanowski (2014) in 2011, and some additional samples from 2013.

#### 3.3.2.3 Field Sampling Procedure

Samples from the shallow groundwater in the riparian area and fen were obtained using a peristaltic pump with Teflon tubing to collect water from piezometers, wells, and from shallow pore waters. Samples were collected into sterile 250 mL PETG sample bottles for groundwater samples, while surface water was collected in 500 mL PETG sample bottles to provide for analysis of both the filtered and unfiltered fraction. These were environmentalized three times prior to filling. All samples were handled according to the EPA Method 1669 “clean hands, dirty hands” protocol for ultra-trace sampling. Field duplicates and blanks were collected periodically for QA/QC.

#### 3.3.2.4 Laboratory Sample Handling Procedure

After collection, Hg samples were stored at 4˚C for a maximum of 48 hours prior to filtering and preservation. In the laboratory, the field sample was filtered and split to be stored for separate analyses. The samples were vacuum filtered into clean 250 mL PETG bottles using an acid-washed PTFE filter apparatus, gloves were changed and the filtering apparatus rinsed with deionized water between subsequent samples. In this apparatus we used 0.45 μm nitrocellulose membrane filters. A portion of the filtered sample was decanted to be stored for DOC and major ion analysis in 60 mL HDPE bottles. The DOC samples were frozen directly while the Hg samples were acidified to 1% v/v with OmniTrace Ultra™ concentrated hydrochloric acid, double-bagged and frozen. Filter and acidification blanks were also taken periodically to ensure clean technique was used throughout.

### 3.3.2.5 Water Sample Analysis

Samples were analyzed at Western University (London, Ontario). Dissolved Organic Carbon was analyzed using an OI Analytical 76 Aurora 1030W TOC (Minimum Detection Limit= 0.2 mg/L). Hg analysis was performed using Tekran 2600 and 2700 Hg instruments for THg and MeHg respectively, according to EPA methods 1631, and 1630. The lowest calibration standards used for total Hg and MeHg were 0.1 ng/L and 0.02 ng/L respectively, and these are considered the lower limits of quantification for this study. All blanks had non-quantifiable concentrations of DOC, THg, and MeHg. Duplicates and spikes were included regularly in the analysis for QA/QC. If duplicates were not within 30% of each other, selected samples from that run were rerun to determine the reliability of that run. Duplicates with quantifiable concentrations were consistent within 30%. However, some of the field duplicates collected had barely/non-quantifiable concentrations of Hg, and these had less consistency between duplicates.

Measurements below the quantification limit are obviously less precise and reliable. However, despite the lower precision and quality of data below the quantification limit, we did not censor our data based on the argument that information on trends may be lost by censoring (Gilliom *et al.*, 1984; Porter *et al.*, 1988). To address the problem of poorly quantified data we report median values and interquartile ranges in boxplots as opposed to averages and standard deviations, because the precision of the median will not be influenced by the poorly quantified data if at least 50% of the data is above the quantification limit (Helsel, 1989). However, the poorly quantified data does influence the precision of the load and flux calculations, which must therefore be considered estimates.

### 3.3.3 Load Calculations

Linear regressions were calculated using GraphPad Prism version 5.00 for Windows, GraphPad Software, (San Diego California USA, www.graphpad.com) to test relationships between flow and DOC/Hg concentrations. The total loads were calculated as the sums of half-hourly discharge data multiplied by the individual sample concentration according to Equation 1, where $C_i$ is the individual concentration estimate that corresponds with the measurement of discharge $Q_i$. Solute concentration estimates for periods between sampling times were calculated by averaging between the samples before and after that period.

$$Load = \sum Ci \times Qi \qquad \text{Equation 3.1}$$

Determining the contributing area for soil pipes is problematic, because they do not have clear topographically defined source areas. Therefore, area-weighted fluxes were calculated, with the same approach that was used by Holden *et al.* (2012) in a peatland catchment. This approach involves calculating a maximum dynamic contributing area (DCA) derived from storm discharge and rainfall data while assuming a runoff coefficient of 1 (Jones, 1997), as shown by Equation 2.

$$DCA\ (m^2) = \frac{total\ storm\ discharge\ in\ pipe\ (m^3)}{total\ storm\ rainfall (m)} \qquad \text{Equation 3.2}$$

The maximum DCA from all storm events recorded was used to calculate area-weighted fluxes. For this analysis only storm events that produced measureable and sustained changes in discharge followed by a return to baseflow conditions were used. In our study four multiple-day storm events with rainfall >15 mm were chosen based on this criteria. Unfortunately since our record only included four runoff-generating storm events, our maximum DCA probably cannot be generalized beyond the monitoring period in question. For the DCA analysis hydrograph separations were calculated with WHAT software using the recursive digital filter method (Sloto and Crouse, 1996). These results were cross-checked with the concave method performed manually (Linsley et al., 1958), in order to choose parameters.

## 3.4 Results

### 3.4.1 Pattern of Solute Concentrations Along the Fen-Stream Continuum

Overall, the highest concentrations of DOC measured in surface and pore waters along the fen-stream continuum were found in the riparian area (Figure 3-2). Based on the entire study period, the median DOC concentration in surface and pore waters in the riparian area (18.5 mg/L) was double that of the fen (9.2 mg/L), while the median stream concentration (15.2 mg/L) was intermediate between these two sources. In the soil pipes and rivulets the concentrations were intermediate between the fen and the riparian area. The median concentration of DOC in the soil pipes (15.0 mg/L) was higher than that in the rivulets (9.8 mg/L) (Figure 3-2).

Similarly, the concentrations of $THg_{FILT}$ were higher in the riparian area compared to the fen. The highest median concentration of $THg_{FILT}$ was measured in the soil pipes. The median concentrations of $THg_{FILT}$ were 0.6 ng/L for the fen, 1.7ng/L for the riparian area, 1.9 ng/L for the soil pipes, 1.1 ng/L for the rivulets and 1.2 ng/L for the tributary.

For $MeHg_{FILT}$ there was nearly an order of magnitude difference between the median concentrations of the fen and riparian area, which were 0.02 and 0.10 ng/L respectively. The highest $MeHg_{FILT}$ concentrations in the riparian area were measured in surface water in one of the near stream depressions where the maximum concentration was 1.24 ng/L. There was considerable variation in concentration even within the riparian area with higher $MeHg_{FILT}$ (as well as DOC and $THg_{FILT}$) concentrations appeared to correspond to the piezometer nests and pools close to those included in GW/OH Group 1 described in Chapter 2, however higher sampling resolution would be needed to confirm this. The median concentration in the tributary (0.05 ng/L) was higher than the fen, but only half the concentration of the riparian area. The median concentration of the rivulets (0.02 ng/L) was roughly equal to the fen, whereas the median concentration in the soil pipes (0.05 ng/L) was approximately double the rivulets' concentration (Figure 3-2).

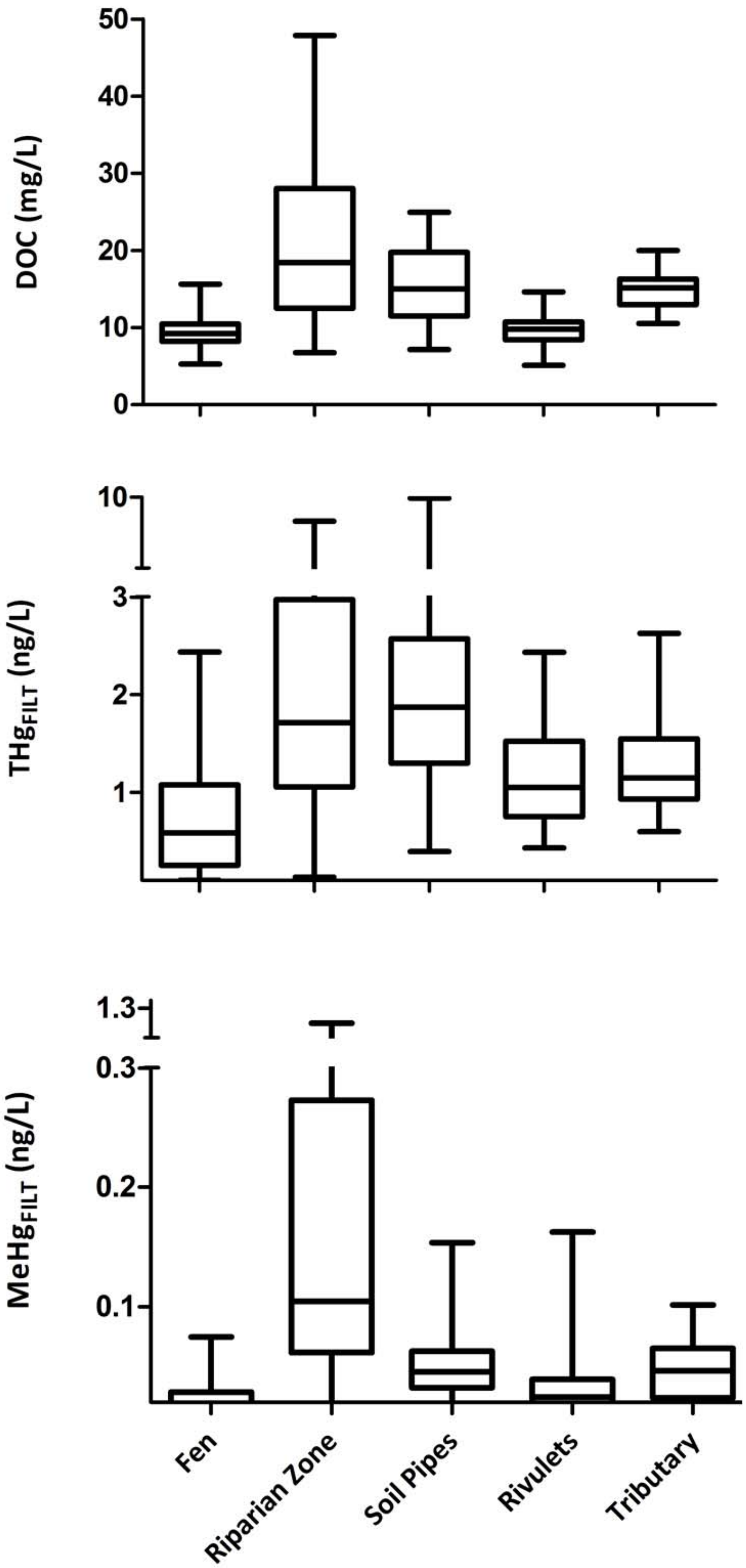


**Figure 3-2: DOC, THg$_{FILT}$, and MeHg$_{FILT}$ concentrations in compartments along a fen-tributary gradient illustrated with box plots where the dark line indicates the median, the boxes extend to the interquartile ranges and the whiskers indicate the minimum and maximum concentrations. Riparian and fen compartments include pore and surface water from pools, while the soil pipes, rivulets and tributary samples are collected from surface and near surface flowpaths. The x-axis intersects the y-axis at the minimum quantification limit for the Hg species (0.02 ng/L for MeHg and 0.1ng/L for THg).**

### 3.4.2 Storm Event Solute Concentrations and Discharge in the Soil Pipes and Rivulet

#### 3.4.2.1 Rainfall and Antecedent Water Table Conditions

The monitoring period commenced shortly after a long dry period in July and records the flow and concentration dynamics within selected surface and shallow subsurface riparian flowpaths (soil pipes and rivulets) as conditions became wetter during the autumn. Only 11 mm of rain fell during the entire month of July, during which the fen water table declined by 15 cm. By mid-July, flow in pipe B and the rivulet ceased, while the very limited flow in pipe A was still sufficient for sampling. After July the quantity of precipitation increased with 58, 69, and 67 mm of rain falling during August, September, and October respectively. As a result, flow in pipe B and the rivulet began again in August and increased throughout the autumn. Higher frequency samples were collected during three storm events in the fall, storm 1, which started on August 4th, storm 3 on September 6$^{th}$ and storm 4 on October 4$^{th}$, these delivered 15.7, 61.2, and 37.4 mm of rain respectively. The antecedent water table position in the fen was different for each of these storm events, it was 4 cm below ground surface for storm 1, at ground surface for storm 3, and 10 cm above ground surface for storm 4.

#### 3.4.2.2 Solute Transport in the Riparian Area During Storm Events in the Fall Monitoring Period

##### 3.4.2.2.1 DOC

In pipe A, the concentration of DOC (Figure 3-3) increased from the start of August until it reached its peak concentration of 17.7 mg/L during the rising limb of storm 3 on Sept 6$^{th}$. During the falling limb of storm 3 (September 10), the concentration dropped down to 1.2 mg/L. Similarly during storm 4 the concentration decreased from 13.2 mg/L on October 4$^{th}$, to 7.2 mg/L sampled on October 17$^{th}$. The flow record was incomplete due to flooding of the weir, which occurred on October 9th. Pipe B not only had a higher median concentration (22.3 mg/L DOC) for the monitoring period compared to pipe A, but also did not reach its maximum concentration (24.9 mg/L) until 23 days later, on September 29. Then, during storm 4, the concentration dropped to its minimum (18.9 mg/L). The rivulet's maximum concentration (12.8 mg/L) occurred on September 9$^{th}$ during the rising limb of storm 3, shortly after pipe A reached its maximum. However, unlike the soil pipes, there was no apparent trend over the season for the rivulet. The range of concentrations (8.3-12.8 mg/L) and median value of DOC (10.3mg/L) in the rivulet closely matched the range of values and median concentrations of DOC in the fen.

##### 3.4.2.2.2 Filtered Hg

In pipe A, the concentration of $THg_{FILT}$ ranged from 0.4 to 3.0 ng/L with a median concentration of 1.3 ng/L over the monitoring period. The maximum concentration occurred during the rising limb of storm 3 on September 6$^{th}$ and subsequently concentrations declined until they reached their minimum on October 4$^{th}$ (Figure 3-3). For pipe A the median $MeHg_{FILT}$ concentration for the fall monitoring period was very low at 0.04 ng/L, as was the maximum 0.06 ng/L that was reached during both storms 1 and 3. Median concentrations of $THg_{FILT}$ and $MeHg_{FILT}$ in pipe B are greater than pipe A (2.3 ng/L and 0.07 ng/L respectively). The maximum $MeHg_{FILT}$ concentration of 0.15 ng/L occurred during storm 3, whereas $THg_{FILT}$ appears to have been diluted during storm events, and the maximum (9.9 ng/L) occurred on September 19$^{th}$ under baseflow conditions. The median $THg_{FILT}$ concentration in the rivulet is lower (0.1 ng/L) than both soil pipes and had no observable seasonal trend. The $MeHg_{FILT}$ concentrations in the rivulet were also low, with a median (0.03 ng/L) that is barely above the quantification limit (0.02 ng/L). Similarly, the median $MeHg_{FILT}$ concentration in the fen was below the quantification limit for the same period. Like the soil pipes, rivulet $MeHg_{FILT}$ concentrations were elevated during storms 1 and 3, reaching a maximum concentration of 0.07 ng/L during storm 3. During storm 4 the rivulet $MeHg_{FILT}$ concentration was diluted to below the quantification limit.

### 3.4.2.2.3 Unfiltered Hg

Unfiltered Hg concentrations, which include the particulate as well as the dissolved fraction, peaked in August for both soil pipes (Figure 3-3). Unfiltered THg and $MeHg_{UNFILT}$ concentrations in pipe A were much lower than for pipe B. The median and maximum concentrations of $THg_{UNFILT}$ were 2.9, 5.8 ng/L and 5.2, 13.5 for pipes A and B respectively, and 0.06, 0.15 and 0.13, 0.70 ng/L $MeHg_{UNFILT}$ for pipes A and B respectively. The maximum $THg_{UNFILT}$ and $MeHg_{UNFILT}$ concentrations for pipe A occurred on August 1; however no flow was recorded at pipe B on this date. The maximum $THg_{UNFILT}$ and $MeHg_{UNFILT}$ concentrations for pipe B occurred shortly after storm 1, when flow had re-initiated in the pipe. During storm 4, $THg_{UNFILT}$ and $MeHg_{UNFILT}$ from both soil pipes were diluted to their minimum concentrations.

For the rivulet, the seasonal trend and maximum values of $THg_{UNFILT}$ and $MeHg_{UNFILT}$ concentrations was generally similar to pipe B; however the median concentrations were lower. For $THg_{UNFILT}$ the maximum concentration (7.0 ng/L) occurred on August 10, shortly after storm 1. The median $THg_{UNFILT}$ concentration for the monitoring period was 2.0 ng/L, which is less than half the median concentration in pipe B. Unlike pipe B, the rivulet did not reach its maximum $MeHg_{UNFILT}$ concentration (0.52 ng/L) until storm 3. The median concentration in the rivulet was nearly the same as pipe A (0.06 ng/L) and similarly to both soil pipes the rivulet was diluted down to its minimum concentration (0.02 ng/L) during storm 4.

### 3.4.2.2.4 Linear Regression Analysis of Flow with Solute Concentrations

Pipe B had weak but significant ($P<0.05$) negative relationships between flow and $THg_{UNFILT}$ and $MeHg_{UNFILT}$, $r^2=0.39$ and 0.30 respectively, with P values of 0.0054 and 0.0173 respectively. The rivulet also revealed significant but weak negative relationships between flow and $THg_{UNFILT}$ as well as $MeHg_{FILT}$, with $r^2=0.37$ and 0.35 respectively and P values of 0.0098 and 0.0191 respectively. The other solutes and pipe A did not have significant relationships between concentration and flow during the monitoring season.

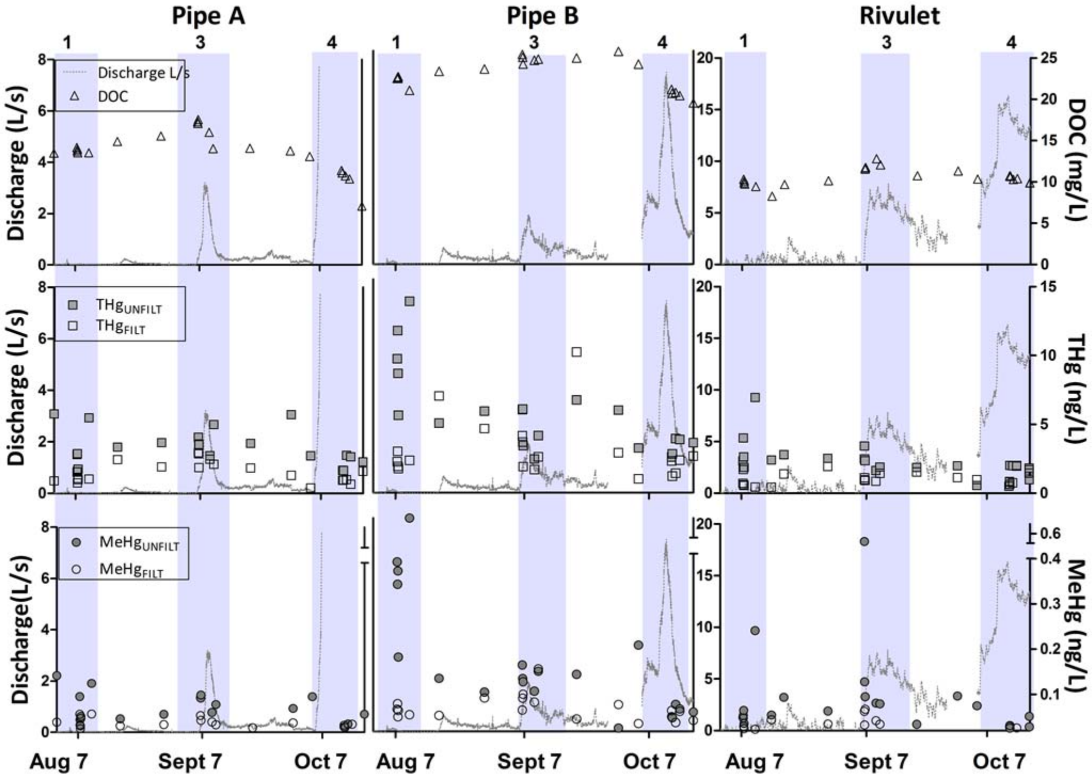


**Figure 3-3: Discharge plotted with DOC, $THg_{FILT}$, $MeHg_{FILT}$, $THg_{UNFILT}$ , and $MeHg_{UNFILT}$ concentrations measured during the autumn monitoring period for pipe B, pipe A and the rivulet. Storm events 1, 3, and 4, during which solute samples were collected with higher frequency are indicated by the grey bars.**

### 3.4.3 Solute Loads

To help quantify the Hg and DOC transported to the stream channel by near stream pathways, solute loads were estimated for the two soil pipes and the rivulet. Unfortunately due to flooding of the weir during the October storm event, pipe A does not have a complete and reliable discharge record for this month. However, since the October storm event recorded peak flow for the season, we did not want to exclude it completely from the analysis. Therefore two sets of load and flux calculations are reported in the sections below. The loads and fluxes were computed until October 4 (65 day monitoring period) for pipe A, pipe B and the rivulet in order to compare between all three sites. In addition, for pipe B and the rivulet only, the loads and fluxes were calculated for the full monitoring period (a 78 day period from August 1- October 17).

#### 3.4.3.1 Solute Loads Estimated for the Period August 1-October 4

The total flows and loads as of October 4th are recorded in Table 3-1. Of the combined flow delivered by the rivulet and two soil pipes, pipe A and pipe B each contribute approximately 10% of the combined flow, while the rivulet makes up the remaining 80%. However, as a result of their higher solute concentrations, the pipes contribute larger proportions of the DOC and Hg loads relative to their contributions to flow. For filtered Hg, pipe B contributed approximately 30-35% of total $THg_{FILT}$ and $MeHg_{FILT}$ loads exported by the two soil pipes and the rivulet,while the rivulet contributed only 50-57%. However, for DOC, the difference between contributions of flow and solute was less; pipe A, pipe B and the rivulet contributed 10%, 20%, and 70% of the combined DOC load respectively. Similarly for both unfiltered Hg species the rivulet contributed 60-70% of the combined load. The pipes and the rivulet differed not only in magnitudes of the overall loads, but also in the proportion of the Hg load that was made up by the filtered fraction. For THg the filtered fraction made up 51, 93, and 64% of the total THg load for pipe A, pipe B and the rivulet respectively. The filtered fraction of MeHg contributed 59, 66, and 30% of the total MeHg loads for pipe A, pipe B, and the rivulet respectively.

#### 3.4.3.2 Solute Loads Estimated for the Period August 1-October 17

The October storm event made a disproportionately large contribution to flow in both pipe B and the rivulet (64 and 55% of total flow respectively). Furthermore it contributed a similar proportion (61 and 53%) of total DOC load for pipe B and the rivulet (Table 3-1). For Hg, the contribution from the final storm was a bit less. For $THg_{FILT}$, the final storm contributed only 40% of the load from pipe B but 51% of the rivulet's final load. For $MeHg_{FILT}$, the dilution was greater in the rivulet during the final storm so the final loads for pipe B and the rivulet were the same (approximately 0.3 mg for both). Fifty-two percent of the total load of $MeHg_{FILT}$ for pipe B was contributed by the final storm event, while only 33% of the total load from the rivulet was delivered. Similarly, the final storm contributed 52 and 42% of total $THg_{UNFILT}$ loads and 61 and 37% of total $MeHg_{UNFILT}$ loads for pipe B and the rivulet respectively.

| | Flow ($m^3$) | DOC (kg) | $THg_{FILT}$ (mg) | $MeHg_{FILT}$ (mg) | $THg_{UNFILT}$ (mg) | $MeHg_{UNFILT}$ (mg) |
|---|---|---|---|---|---|---|
| ***Aug 1-Oct 4*** | | | | | | |
| Pipe A | $1.2x10^3$ | 19 | 2.5 | $4.8x10^{-2}$ | 4.9 | $8.2x10^{-2}$ |
| Pipe B | $1.7x10^3$ | 41 | 7.8 | $1.4x10^{-1}$ | 8.3 | $2.1x10^{-1}$ |
| Rivulet | $1.0x10^4$ | $1.2x10^2$ | 13 | $2.2x10^{-1}$ | 21 | $7.2x10^{-1}$ |
| ***Aug 1-Oct 17*** | | | | | | |
| Pipe B | $4.7x10^3$ | $1.0x10^2$ | 13 | $2.9x10^{-1}$ | 17 | $5.5x10^{-1}$ |
| Rivulet | $2.3x10^4$ | $2.5x10^2$ | 27 | $3.2x10^{-1}$ | 35 | 1.2 |

**Table 3-1: Compares total loads of water, DOC, and THg and MeHg over the monitoring season broken down by site. Two different monitoring periods are illustrated because pipe A is missing the rest of its flow record.**

#### 3.4.3.3 Dynamic Contributing Area and Area Weighted Flux Estimates

The maximum dynamic contributing area (DCA) for pipe B occurred during storm 4. Since Jones (1997) uses the maximum DCA for calculating area-weighted fluxes, the contributing area for our study should be estimated using stormflow from storm 4. Unfortunately the October stormflow records for both pipe A and the rivulet are incomplete, because pipe A was flooded and the rivulet did not return to baseflow within the monitoring period. The partial record for the rivulet allows an estimate of DCA to be made. Since our purpose in calculating area-weighted fluxes is to have representative estimates that can be compared to other studies, we excluded pipe A, and calculated the fluxes for pipe B and the rivulet only.

For storm 4 the partial record for the rivulet indicates that the DCA is at least $3x10^5$ $m^2$. If it is assumed that the DCA of the rivulet increased roughly proportionally with pipe B between storm 3 and storm 4, the maximum DCA for the rivulet can be estimated to be approximately $7x10^5 m^2$. Based on these DCAs the area-weighted fluxes were calculated (Table 2). The mean daily area weighted fluxes for pipe B were up to an order of magnitude larger than those for the rivulet for all solutes (Table 3-2). The difference was greatest for MeHg and smallest for DOC.

| | **$DCA_{max}$ ($m^2$)** | **DOC ($mg/m^2/day$)** | **$THg_{FILT}$ ($ng/m^2/day$)** | **$MeHg_{FILT}$ ($ng/m^2/day$)** | **$THg_{UNFILT}$ ($ng/m^2/day$)** | **$MeHg_{UNFILT}$ ($ng/m^2/day$)** |
|---|---|---|---|---|---|---|
| Pipe B | $6x10^4$ | 20 | 3 | $6x10^{-2}$ | 4 | $1x10^{-1}$ |
| Rivulet | $7x10^5$ | 5 | $5x10^{-1}$ | $5x10^{-3}$ | $7x10^{-1}$ | $2x10^{-2}$ |

**Table 3-2: Compares average daily area-weighted fluxes estimated for DOC, THg and MeHg between pipe B and the rivulet.**

## 3.5 Discussion

### 3.5.1.1 Solute Concentrations in the Fen-Stream Transition

Peatlands are known to contribute MeHg to downstream aquatic systems (e.g. St Louis *et al.*, 1994; Bishop *et al.*, 1995; Branfireun *et al.*, 1996; Grigal, 2002). However, as observed by Ulanowski (2014), the fen at our study site has very low MeHg concentrations (typically close to quantification limits). The median concentration for pore and surface water in the fen of 0.02 ng/L is much lower than those observed at other peatland sites in Ontario's Canadian Shield area where mean pore water concentrations can be more than an order of magnitude higher ~ 0.4-0.6 ng/L and maximum concentrations can be nearly two orders of magnitude higher ~7-10 ng/L (Heyes *et al.*, 2000; Mitchell *et al.*, 2008). At our site the riparian area has elevated concentrations of DOC, THg and MeHg, relative to the fen. Our median $MeHg_{FILT}$ concentration in the riparian area of 0.10 ng/L is still low compared to the other peatland sites in general. However, it is comparable to another riparian zone in Sweden where pore water typically had MeHg concentrations ≤ 0.2 ng/L for depths below 10cm, with higher concentrations in the surface layer of soil (0.3-1.5 ng/L) and in living moss (>2ng/L) (Bishop *et al.*, 1995).

The riparian environment at our site is intermediate between the fen and what might be more typical of an upland forest based on the vegetation cover, thinner organic layer (~0.5m compared to 2m), lower water table elevation, and steeper slope. Other studies have identified boundaries between upland and wetland environments as zones of elevated Hg export and methylation (Kolka *et al.,* 2001; Mitchell *et al.*, 2008; Mitchell *et al.*, 2009). In their study of two peatlands within the Marcell Experimental Forest Mitchell *et al.* (2009) recorded the highest concentrations of MeHg along the peatland-upland interface and found that flow from the upland areas brought $SO_4^{2-}$ and labile DOC to the interface (Mitchell *et al.*, 2008). These imports of labile DOC are important because despite deep accumulations of carbon in peatlands, labile DOC is often limited in peatlands (Updegraff *et al.*, 1995; Mitchell *et al.*, 2008). Kolka *et al.* (2001) identified the hydrologically active perimeter (lagg) of a bog as an important source of Hg because flowpaths from the nutrient rich upslope with more labile carbon and flowpaths from the nutrient poor bog intersect there. At our site, the shallower depth of organic matter in the riparian area compared to the fen allows for greater interaction with the underlying shallow groundwater. Therefore there were greater concentrations of major ions in the shallow organic layer compared to the fen (Chapter 2). Furthermore the different types of vegetation that grow closer to the stream potentially provide a source of more labile carbon than is found in the fen. Other studies have identified that maximum MeHg concentrations can be found in the zone of fluctuating water table (Heyes *et al.,* 2000; Branfireun and Roulet, 2002; Branfireun, 2004). In chapter 2 we observed a greater amplitude and rate of water table fluctuations in the near stream depression compared to the fen, potentially resulting in alternation between anaerobic and aerobic conditions and thereby promoting methylation.

The disproportionate importance of riparian areas as solute sources to streams relative to their spatial extent has been widely recognized (Vidon *et al.*, 2010). Furthermore, Bishop *et al.* (1995) identified riparian wetlands as zones of elevated Hg methylation. Our results suggest that this might hold true in the wetland-dominated landscape of the HJBL, even though the riparian area at our site is different from most riparian areas in the literature because water is transmitted to it from a peatland rather than a hillslope; and it therefore compares differently to its terrestrial catchment.

McClain *et al.* (2003) define "hot spots" as discrete locations within the landscape where biogeochemical reactions occur at disproportionately high rates. These hot spots are often located in transitional areas between terrestrial and aquatic ecosystems where convergent hydrologic flowpaths facilitate mixing of waters transporting complimentary reactants (McClain *et al.*, 2003). Concentrations of MeHg in our study were highest in the near stream depression wetlands with pooled water adjacent to the stream channel. During episodes of very high stream flow, surface flooding may directly connect pools to the stream. Under lower flow conditions the main connection appears to be via flow in soil pipes.

The soil pipes had DOC, $THg_{FILT}$, and $MeHg_{FILT}$ concentrations that are higher than the rivulet, which had concentrations that closely matched those of the fen. By contrast the soil pipes had concentrations that were in between the fen and the organic horizon and pools in the riparian area. This supports the inference that the rivulets are more hydrologically connected to the fen than the soil pipes (Chapter 2). The relatively lower $MeHg_{FILT}$ concentrations in the soil pipes compared to the median for the riparian area might reflect greater heterogeneity of $MeHg_{FILT}$ concentrations in the riparian zone relative to DOC and THg.

#### 3.5.1.2 Temporal Trends and Storm Events

Whereas elevated concentrations may be observed during storm events early in the fall, those storms occurring later in the season appear to result in more dilute concentrations, suggesting that the relationship between flow and concentration for DOC and Hg species at our site is confounded by broader seasonal trends. This explains the weakness of the regression relationships between flow and concentration. Furthermore, it clarifies why negative correlations were found despite the observation that in general, concentrations are elevated during storm events. Other studies have similarly observed weak regression relationships between flow and Hg concentration despite noting elevated concentrations during storm events (Bushey *et al.*, 2008; Schuster *et al.*, 2008; Shanley *et al.*, 2008; Demers *et al.*, 2010). The seasonal trend data is consistent with there being a small local source for DOC, MeHg, and THg that can be exhausted fairly quickly, and which was flushed over the course of the autumn.

Although concentrations were generally lower at the end of the autumn, the final storm event in October contributed a disproportionately large proportion of the total solute loads. This was especially true of pipe B, where the event response for storm 4 contributed more than 60% of the season's loads for some solutes, despite comprising only 17% of the monitoring period. Our results support previous work that has identified the disproportionate importance of storm events, or other short-term episodes of elevated flow for Hg export (Branfireun *et al.*, 1996; Babiarz *et al.*, 1998; Mitchell *et al.*, 2008). However, since storm 4 also represented ~60% of seasonal flow for pipe B and the concentrations were diluted during the storm event, the increased stormflow load in late autumn appears to be driven by flow rather than changes in water chemistry.

In our study the peak concentrations for filtered Hg generally didn't coincide with the peak concentrations for unfiltered Hg, suggesting that the dynamics of the particulate fraction of Hg may be controlled by different mechanisms than the dissolved fraction. There was also variation between the different sites, with very high concentrations occurring in early August for pipe B, but not pipe A. The complete cessation of flow in pipe B during the dry period in July was likely the cause of the high unfiltered Hg concentrations recorded once flow resumed in August. The lack of flow would have allowed eroded material to accumulate there, ready to be mobilized once flow started again. By contrast flow in pipe A continued through the dry period, so eroded material would not have had the same opportunity to accumulate inside this soil pipe. Similarly Holden *et al*. (2012) found that particulate organic carbon loads were almost double in ephemeral pipes compared to perennial pipes and they also attributed this to the potential for particulate matter to build up during dry periods. Although sediment loads were not estimated at our site, high sediment accumulation was observed near both pipe outlets, indicating that pipes may transport significant sediment loads, especially under high flow. In other peatlands, soil pipes have been shown to transport up to 430 kg of sediment annually (Jones, 2004). At our site the eventual fate of the sediment transported by soil pipes is uncertain and requires further research to test if localized deposits of this particulate MeHg load would be a potential pathway for MeHg into the aquatic food web.

### 3.5.1.3 Area Weighted Fluxes

#### 3.5.1.3.1 DOC

Our estimate of DOC fluxes from the rivulet at 5 mg/m$^2$/d, is close to Ulanowski's (2014) estimate for the fen of 3 mg/m$^2$/day for the ice-free season of 2011 May 15-Oct 19. This flux of DOC from the fen was lower than fluxes of DOC measured from other peatland environments (Ulanowski, 2014). Both the rivulet and fen estimates are much lower than our estimate for pipe B of 20 mg/m$^2$/d. This makes sense considering the rivulet is more directly connected to the fen, whereas pipe B is more connected to the riparian area, where the source area concentrations are higher (Chapter 2). Our estimate does not include the earlier part of the ice-free season, and is likely biased by higher concentrations of DOC in the autumn compared to the spring. Furthermore interannual variation may also be driving the differences; however the concentrations we observed in the fen during 2012 were similar to the concentrations reported by Ulanowski (2014) during the August to October period in 2011.

Our study suggests soil pipes are important means of transport for DOC in this landscape. Similarly, Holden *et al.* (2012) found that soil pipes contributed 20% of the total load of DOC exported by a stream draining a blanket peat catchment. Our results support their conclusion that soil pipes can have a significant role in carbon transport within peatland dominated watersheds. Holden *et al.* (2012) report DOC fluxes from soil pipes in a blanket peat catchment ranging from 20-70 mg/m$^2$/day. Our estimate of average flux, 20 mg/m$^2$/day falls at the bottom of this range. However, as a result of the higher peak flow in pipe B (7.2 l/s) compared to maximum peak flow reported in the blanket peat catchment (3.8 l/s) (Smart *et al.*, 2013), our total load of DOC for pipe B was significantly larger than the total loads reported by Holden *et al.* (2012). The total DOC load from pipe B (Aug 1-Oct 17) was 100 kg, while the maximum annual load reported by Holden *et al.,* (2012) was 77.43 kg. This might be because our maximum estimate for DCA for pipe B (60,000 m$^2$) was an order of magnitude higher than the (6151 m$^2$) max DCA reported by Smart *et al.* (2013), suggesting pipe B might have a larger area to supply DOC from as well as higher volumes of flow compared to the soil pipes in the catchment reported by Holden *et al.* (2012).

### 3.5.1.3.2 Mercury

As we found for DOC, our average estimated THg and MeHg fluxes from pipe B are larger than those estimated by Ulanowski (2014) from the nearby fen, suggesting that the riparian area plays an important role in both carbon and Hg export. For THg, our average flux for pipe B and the rivulet were 4 and 0.7 ng/m$^2$/day, whereas he reported 0.33 ng/m$^2$/day for the fen. Likewise our average total MeHg flux of 0.1 ng/m$^2$/day for pipe B was an order of magnitude higher than his flux of 0.012 ng/m$^2$/day for the fen. The MeHg flux from the rivulet was much closer to that of the fen, exporting 0.02 ng/m$^2$/day.

The THg flux from pipe B of 4 ng/m$^2$/day, falls in the lower end of the range reported in other wetland dominated watersheds in Ontario, the Adirondacks, and Sweden, which range from 1.6 ng/m$^2$/day (St. Louis *et al.*, 1994) to 16 ng/m$^2$/day (Selvendiran *et al.*, 2008) THg. Our MeHg flux from pipe B was similar in magnitude to those exported from a beaver meadow wetland in the Adirondacks with net fluxes of 0.09 ng/m$^2$/day MeHg (Selvendiran *et al.*, 2008), and significantly greater than what they observed from a riparian peatland in the same watershed (0.03 ng/m$^2$/day MeHg) (Selvendiran *et al.*, 2008). By contrast, the fluxes in some Ontario wetland-dominated catchments can be more than an order of magnitude higher, such as 1.5 ng/m$^2$/day MeHg from St Louis *et al.* (1994). While our estimates for pipe B Hg fluxes fall within the low end of the ranges for Hg export observed in other wetland-dominated environments, the fluxes from the fen and rivulet are much lower than those observed in other watersheds.

### 3.5.1.4 Riparian Hot Spots and Moments of Hg Transport

Hot spots and moments may refer to transport of solutes as well as biogeochemical rates, which reflects the potential for elevated transport along localized preferential flow paths, or for short durations of time such as storm events (Vidon *et al.*, 2010). We argue that pipe B, and potentially other soil pipes in the riparian area are hot spots of transport for THg, MeHg and DOC. Since only 17% of the monitoring period (during the final October storm event) contributed 50-60% of the total solute load for pipe B, we suggest that the soil pipes also experience hot moments of transport (Vidon *et al.,* 2010) during large storm events, driven mainly by flow, in these hydrologically responsive features. In blanket bogs in Britain, Holden *et al.* (2012) found that soil pipes could be significant point sources of DOC, and our research supports this finding and furthermore suggests that in parts of the HJBL soil pipes in the riparian area may also be important point sources of MeHg and THg.

## 3.6 Conclusions

Our work highlights the role of the riparian area in mediating biogeochemical connectivity between the fen and the stream. Compared to the fen, one of the soil pipes transported elevated concentrations of DOC, THg and MeHg. While the filtered carbon and Hg loads in the rivulet were mostly consistent with concentrations in the fen, the rivulet transported elevated loads of particulate MeHg; likely as a result of erosion. This modification of solute exports from the fen, by mixing with or eroding the riparian area, is an example of the gatekeeper role of riparian zones described in other environments (Burt, 2005). Given the exploratory and small scale nature of this study, we also recommend higher resolution sampling of the riparian area over broader spatial and temporal scales to determine whether these results are consistent and have landscape scale significance.

Higher concentrations and fluxes of DOC, THg, and MeHg were found in parts of the riparian area, when compared to the fen. Localized MeHg hot spots in the riparian zone are likely to be missed by most larger-scale sampling regimes, especially when sampling efforts are focused on peatland features as the expected sources of MeHg. We suggest that future sampling for MeHg should include samples from pools and the organic horizon in the riparian area. Furthermore, transport of DOC, THg and MeHg was found to be weather sensitive, since the fall loads for pipe B and the rivulet were dominated by a single storm event. Mercury methylation was found to be localized even within the riparian area, with a wide range of concentrations in shallow pore water and surface pools between different sampling locations in the riparian zone. Furthermore, overall Hg and carbon transport were not only localized, but episodic, with late autumn storm events playing a particularly important role. Soil pipes play an important role in DOC and Hg transport, especially during storm events, however these features would commonly be missed in broad-scale studies of the landscape. These complexities highlight the difficulty of quantifying Hg and DOC dynamics within this landscape, and our results could help inform future sampling efforts to better capture them.

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# 4 Conclusions and Future Work

The general objective of this thesis was to improve our understanding of hydrological connectivity between peatlands and headwater streams in the peatland-dominated HJBL of the Canadian subarctic, as well as to determine the implications of hydrological connectivity for runoff biogeochemistry. Specifically we were interested in the hydrological export of DOC, THg and MeHg from the peatlands to nearby aquatic habitats. This kind of baseline information is critical in order to recognize changes to these patterns as a result of future climate or land-use change.

The outcomes reported by this thesis are limited by the relatively sparse spatial and temporal frequency of the pore water samples, as well as the intensive monitoring season being limited to one study season, making it hard to know if the results are representative. This study is to some extent a preliminary work as the field site had not been described extensively previous to the beginning of the field season presented here. The soil pipes, riparian depressions, and additional rivulets were mapped during this early part of the field season, and initial study objectives shifted to reflect the inferred importance of these features for governing connectivity in this landscape. The conclusions presented here could be significantly strengthened with further research on the hydrological and biogeochemical characteristics of riparian areas in the Central James Bay Lowland to determine if the features and processes observed in this study occur in riparian areas elsewhere in this landscape or are unique to this specific site. Higher spatial and temporal resolution sampling of riparian organic soils might identify other Hg methylation hot spots, or reveal patterns that this study failed to capture. Specifically it is possible to speculate a relationship between interaction of shallow groundwater with the organic soil and elevated Hg methylation, as observed by Branfireun and Roulet (2002) in a different wetland environment, however in this study the spatial resolution of sampling within the riparian area was inadequate to draw such conclusions firmly. Although the samples were not high enough resolution to confirm a relationship, our results hinted at a potential relationship between different groundwater sources and the concentration of MeHg, suggesting this may be an important avenue of further research. Furthermore we identified particulate Hg transport as an important aspect of the overall Hg budget for the soil pipes and rivulet however, particulate carbon and sediment loads were not directly measured, and erosional processes in these features are not sufficiently well described. Furthermore the eventual fate of this particle-bound Hg and the relevance of the point sources we identified to the aquatic ecosystem are both poorly understood.

The accuracy of our flux estimates for dissolved organic carbon and Hg were limited by the shortness of the monitoring period, samples that were below the quantification limit, and the absence of topographically defined contributing areas for the soil pipes and rivulets, forcing us to rely on an approximation based on an estimated maximum DCA calculated from flow and precipitation data. Furthermore this estimate was based on a very small number of storms, and cannot be considered representative for more than the short monitoring period. Our flow measurements were also only calibrated for a similarly short period of time, hindering their reliability, which was further impeded by technical failures and flooding of one of the weirs. Longer term monitoring of a larger number of soil pipes and rivulets could facilitate more representative and accurate estimates and a better understanding of the range of possible flows and solute fluxes from these features. Better estimates of the overall contribution from soil pipes might be accomplished by using more sophisticated methods, for example geophysical techniques such as GPR (Holden, 2004) to map their networks, and potentially better quantify their contributing areas. The understanding of storage capacity in the near stream depressions might be more realistic if it included unsaturated as well as saturated zone stored water.

This study drew on the intersection of several themes in the literature focusing on; riparian zones, soil pipes and other preferential flowpaths, carbon and mercury biogeochemistry in peatlands, and recent research on runoff generation and connectivity in northern catchments, and more specifically it builds on recent research efforts focused in the HJBL, a unique and ecologically significant landscape.  Our research agreed with recent literature that suggests the importance of storage thresholds to runoff generation in many northern catchments (Frisbee *et al*., 2007; Spence *et al*, 2007; Woo and Mielko, 2007; Spence, 2010; Spence *et al*., 2010; Oswald *et al*., 2011; Phillips *et al*., 2011). This threshold behaviour can result in strong seasonal variation in hydrological connectivity such as has been observed in other peatland environments (eg. Quinton and Roulet, 1998). However, Orlova and Branfireun (2014) found that the peatland contribution to the stream network remained fairly consistent throughout the year, whereas the proportions of groundwater and precipitation change. In the context of our results this suggests that under wet, connected, conditions precipitation and snowmelt may be transported directly to the stream networks via the preferential flowpaths, and experience minimal mixing with stored water in the fen and riparian areas. Furthermore, our results suggest that the groundwater chemical signature may not purely reflect baseflow contributions, but also represent some proportion of soil pipe discharge since this transports mixed water from the riparian zone. The groundwater signal in the water from the soil pipes would change seasonally since under wetter conditions the soil pipes deliver water with a chemistry that is more similar to the dilute fen.

The main contribution of this thesis is to highlight the disproportionate biogeochemical and hydrological importance of the small riparian areas of the Central James Bay Lowland, and suggest that these areas be explicitly included in future sampling regimes and modelling efforts in this region. Our observations are in agreement with a growing body of literature on the biogeochemical and hydrological importance of riparian zones in diverse contexts, and particularly the potential for occurrence of biogeochemical hot spots and moments within the terrestrial-aquatic interface (Vidon *et al*., 2010). This study also identified the important hydrological role of small preferential flowpaths that could easily be overlooked in large-scale surveys of the landscape, and therefore suggests the importance of including some detailed process-oriented studies in such environments.

The threshold mediated nature of runoff generation in preferential flow paths in the riparian areas may indicate greater sensitivity to climate change as suggested by Carey *et al*. (2010). Furthermore, climate change could directly influence the development of soil pipes and rivulets since increased precipitation might result in greater erosive power, and extreme weather events have been observed to have significant impact on the geomorphology of pipe networks in other peat-dominated landscapes (Holden *et al*., 2012). Furthermore, intensified drying and cracking may occur as a result of enhanced evapotranspiration, influencing soil pipe networks. In some blanket peat catchments, an increase in the proportion of flow as pipeflow and soil pipe density has been observed as a result of draining of the peatland (Holden *et al*., 2006). Although our site is located in a very different landscape it is therefore possible that drier summer conditions may promote soil pipe development. Increased temperatures might also stimulate biogeochemical activity, increasing the concentrations of DOC and MeHg exported from the riparian area by soil pipes. Enhanced soil pipe development could potentially influence both the chemistry of the water delivered to the stream as well as likely shifting towards a more hydrologically responsive stream hydrograph for the main channel, with higher and shorter peaks than presently observed since soil pipes facilitate relatively rapid runoff generation. Alternately, more extreme drying of the climate might reduce rivulet and pipe flow if water levels in near stream depressions and the fen failed to meet threshold levels even during the fall and spring. This would likely significantly impact the quantity and quality of water reaching the stream channel. Although drier conditions are one scenario expected for this region, alternate consequences of future climate change are possible. For instance increased temperatures coupled with increased precipitation concentrated in the winter might result in a more extreme hydrograph with wetter conditions in the spring and drier conditions over the summer, such enhanced cycles of wetting and drying might promote mercury methylation in the near stream area, but could rely on a rewetting during the fall for transport to the stream. Alternately if conditions became uniformly wetter, greater connectivity with the fen might be expected resulting in generally more dilute chemistry overall.

Our findings could assist with developing a better targeted sampling regime for MeHg that includes higher frequency sample collection during storm events, since storm events represented a significant portion of solute loads delivered to the stream during our study. Specifically storm events in the fall are important for MeHg transport to the streams, and could be specifically targeted. In the context of land use change, understanding the nature of hydrological connectivity and dominant flow paths between fens and streams could also be relevant for guiding management practices in this landscape to help prevent any potential releases of contaminants. For example, although our results indicate that the riparian zone mediated hydrological and biogeochemical connectivity between the fen and the stream, the rivulets provided localized pathways that mostly bypassed the riparian area, and delivered fen water directly to the stream channel. This would reduce the ability of the riparian zone to act as a buffer zone for any contamination in the fen during the period when fen water tables are high enough for the rivulets to be hydrologically connected.

Finally, as a preliminary and exploratory study, this thesis suggests future avenues of research such as performing higher resolution sampling of MeHg in the riparian area to identify the complex spatial patterns hinted at by this study and determine any potential link to differences in shallow groundwater chemistry as a potential driver of variability in Hg methylation. This might prove to be a very useful link, should it prove to be consistent and significant, since it might facilitate some prediction of the expected distribution of higher MeHg concentrations based on mapping the different shallow groundwater sources, which seem to have notably different chemistries. Another important avenue of study would be aquatic ecology work focused on identifying pathways for MeHg to enter the aquatic foodweb, which explicitly considers the possibility that particle-bound MeHg in sediments deposited near soil pipe and rivulet outlets represents a potential point source, and determining whether this is an effective pathway for uptake by aquatic organisms. This could be combined with directly quantifying the sediment loads transported by the soil pipes, and more precise assessments of the degree to which this material accumulates at the soil pipe outlets, or if it can be remobilised. Furthermore, other erosional stream processes, such as slumping of stream banks, may be alternate sources of particle-bound Hg to the aquatic ecosystem, and may be important considering the elevated concentrations of MeHg in the riparian area compared to the fen.

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# Curriculum Vitae

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|---|---|
| **Name:** | Meghan Kline |
| **Post-secondary Education and Degrees:** | Simon Fraser University<br>Vancouver, British Columbia, Canada<br>BSc. Hon. Earth Sciences |
| | Western University<br>London, Ontario, Canada<br>MSc. Candidate Earth Sciences |
| **Awards:** | Campbell Scientific Award for Best Student Poster in Hydrology. Saskatoon, SK. Spring, 2013. |
| **Related Work Experience:** | Teaching Assistant<br>The University of Western Ontario |
| | Research Assistant<br>The University of Western Ontario (DeBeers Victor Mine) |
| | NSERC USRA Grant Holder<br>Simon Fraser University |
| **Conferences and Workshops:** | Joint Scientific Congress (CMOS, CGU, CWRA): Bridging Environmental Science, Policy and Resource Management. Saskatoon, SK. Spring, 2013 |
| | Mer Bleue Annual Science Workshop. Montreal, QC. Winter, 2013 |